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Lanthanide Mediated Activation of C-H and C-X Bonds

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Contents

Chapter 1

General Introduction

Trends in Organometallic and Metal Mediated Organic Chemistry. In contemporary chemistry we see clearly a need for more selective processes, stimulated by more severe environmental and economic demands.[1] Because of this growing need for processes which make more effective use of raw materials and produce less salt, there is a strong interest in the field of catalysis. At present organometallic and coordination chemistry have reached a high level of sophistication and they are used more and more to perform selective transformations both in the field of specialty chemicals and in bulk synthesis.[1] Even when metal compounds are not used as catalysts, they can function as templates for selective transformations. In this case the term 'metal mediated' is often used to indicate that the reaction is tuned or facilitated by a metal complex.

Some of the largest industrial bulk processes today are based on organometallic catalysts.[1,2] Representative examples are the bulk synthesis of polyethylene and polypropylene using 'third generation' Ziegler-Natta catalysts and the hydroformylation of olefins catalyzed by homogeneous cobalt and, sometimes, rhodium complexes. Another large scale industrial process is the Shell Higher Olefin Process (SHOP) in which the oligomerization catalyst is a homogeneous nickel complex. However, particularly in the field of fine chemicals, homogeneous metal catalysts are required to achieve enantioselective transformations. The development of these optically active catalysts is a special challenge.

Unique Properties of Group 3 Organometallics. The chemistry of group 3 and lanthanide metals is characterized by their high Lewis acidity, which is caused by the low ionization energies of these metals and results in their tendency to reach high oxidation states.[3] As a consequence Ln-C and Ln-H bonds (Ln = group 3 or lanthanide element) are highly polarized with partial negative charge located on the α-C or hydride ligand. Very often the reactivity of these bonds resembles that of carbanion and hydride chemistry associated with the alkali and alkaline earth metals. Due to their common +3 oxidation state, these metals have a wealth of coordination

chemistry, which is enhanced by the very large ionic radii compared to other transition metals and results in large coordination spheres. The coordination of auxilary ligands can have significant effects on the Ln-H or Ln-C bonds. In addition, by interacting with an approaching reagent, the ligand system can induce a specific orientation of the incoming molecule and therefore control the way in which this molecule reacts with the Ln-H or Ln-C bond.

The presence of five empty and relatively low lying d-orbitals makes these complexes very electrophilic and, as a result, they complex Lewis bases very easily. In fact even the electron density of C-H bonds and salts like alkalihalides can be used to decrease the electron deficiency of the metal center. The 3-center 2-electron intramolecular coordination of C-H bonds is now very generally known, especially for the group 3 metals and lanthanides. The term 'agostic interaction' is used for this effect.[3a]

The high affinity of group 3 centers for electron density also results in Ln-X (X = hetero-atom) bonds with large bond dissociation energies (BDE). Thermochemical measurements have revealed that Ln-X bonds are among the strongest known.[4] Consequently the formation of Ln-X bonds in catalytic processes often leads to deactivation of the catalyst. Because of the close similarities in size and ionization potential of the metal centers the chemistry of the individual lanthanides, plus yttrium and even scandium, is very related, although minor differences in size and relative energies can have dramatic effects on product distributions as will be demonstrated later on in this thesis. In our study we focus mainly on the smaller congener yttrium, which is considered to be a good representative for group 3 metals and lanthanides. In a few cases we will include lanthanum and cerium to illustrate the influence of larger ionic radii.[5]

Not surprisingly, due to the unique properties of the group 3 metal complexes, the chemistry related with them is rather unique as well.

Some Important Elementary Processes on Group 3 and Lanthanide centers. Since +3 is the common oxidation state for lanthanides,[6] redox reactions are in general not observed. For instance the two electron processes oxidative addition and reductive elimination, which pervade late transition metal chemistry, do not take place at these metal centers. Instead the chemistry is dominated by concerted four-electron four-center processes also named σ-bond metathesis.[7] One of the first studied reactions of this type is the activation of C-H and H-H bonds.[3a] The transition states involved are cyclic and four-centered as is shown in Figure 1A. In a

concerted manner the M-R bond and the R'-H bonds are broken and two new bonds, M-R' and R-H, are formed. The activation energies involved are rather low (typical values: ΔH = 10 - 20 kcal/mol, ΔS = -20 - -40 eu) because of the pool of metal acceptor orbitals available which stabilize the transition state. Also the migratory insertions of olefins and alkynes into Ln-R bonds proceed through σ-bond metathesis transition states (Figure 1B).

The discovery of the elementary reactions described above has led to a wealth of catalytic processes. Some of the most exciting examples will be discussed here.

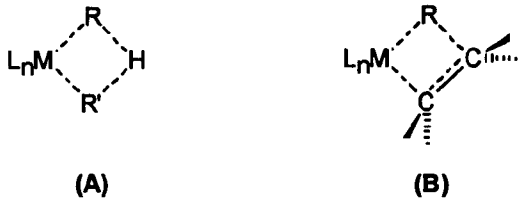

Figure 1. σ-Bond metathesis transition state for C-H activation (A) and olefin insertion (B) with a metal complex L_nMR (R = H or hydrocarbyl).

Catalytic Processes Based on Group 3 Organometallics. Lanthanide complexes have been studied by Watson as models for Ziegler-Natta olefin polymerization and it was found that all the fundamental steps take place on these metal centers.[8] Later Marks *et al.* found that lanthanide hydride complexes are the most active homogeneous systems for catalytic hydrogenation of olefins.[9] The turn-over frequencies (TOF) are comparable with those of commercially used heterogeneous systems. In our group the dimerization of terminal alkynes was developed by Den Haan[10] and Heeres.[11] Also cyclization polymerization of dienes using scandium systems shows that group 3 and lanthanide metals can induce spectacular transformations of substrate molecules under generally very mild conditions.[12] Without exception these studies were based on olefins without hetero-atoms which makes these systems of limited use for synthetic and/or industrial applications.

A severe drawback of these group 3 and lanthanide based catalytic cycles is that in addition to their water and oxygen sensitivity, they are also sensitive towards functionalities in the substrate molecule. Often substrates which contain a functional group are not tolerated by the lanthanide catalyst and cause rapid deactivation through Ln-X bond formation. This explains the large number of studies based on

hydrocarbons and the relatively few directed towards the conversion of susbstituted molecules.

We now see the development of more selective processes originating from the early work described above. Asymmetric hydrogenation[13] and stereoregular olefin polymerization[14] are good examples of this trend. Also the catalytic conversion of more complicated substrates containing functionalities is a matter of increased interest. For instance the hydrogenation of unsaturated ethers and sulfides has received attention lately[15] as well as the cyclization-polymerization of functionalized dienes[16]. Cyclization reactions of unsaturated amines[17] and hydroboration of olefins[18] also show that in some cases functional groups are tolerated. Even polymerization of methylmethacrylate can be achieved in a living fashion despite the chemically active carbonyl and COR groups in the monomer.[19]

Another aspect which could become very important for the area of metal mediated organic synthesis is C-H activation and subsequent functionalization of the M-C bond formed. Since Lewis-acidic early transition metal complexes, especially the group 3 metals and lanthanides, are very active in C-H activation, it would be interesting to put this reaction to synthetic use. For instance the migratory insertion of unsaturated molecules into the M-C bond formed by C-H activation has been studied. Jordan and co-workers have shown that this procedure can be used to functionalize pyridines in the 2-position.[20] Also studies by Buchwald on functionalization of arenes mediated by group 4 benzyne complexes are based on this approach.[21] Until now these studies have been limited to group 4 metals and no examples of lanthanide systems have been reported.

Goal and Survey of this Investigation. The goal of this research was to extend group 3 and lanthanide organometallic chemistry to the activation of molecules containing functional groups. We feel that a better understanding of the interaction of lanthanide carbyls and hydrides with hetero-atom containing molecules can ultimately result in catalytic conversions of these molecules.

Chapter 2 begins with a mechanistic investigation of C-H activation reactions of the yttrium hydride complex $(Cp^*_2YH)_2$ in aliphatic and aromatic solvents to get a better understanding of the types of C-H activation possible with non-hetero-atom containing molecules. In chapter 3 the results of chapter 2 are supported by an MO computational study at the extended Hückel level which shows that H/D scrambling and metallation of arenes are different processes. Then we turn our attention to productive activation of hetero-atom containing substrates (chapters 4-6). By

selective metallation of pyridine and subsequent reactions with the metallation product Cp^*_2Y(2-pyridyl), we were able to perform a number of interesting functionalizations at the pyridyl ring (chapter 4). The nitrogen atom of the pyridyl ring functions as directing group both for C-H activation and subsequent functionalization. In chapter 5 other hetero-atom containing substrates like ethers and sulfides are studied and it was found that C-X activation resulting in formation of Cp^*_2LnX is important with these molecules. Finally in chapter 6 we focus on interactions with esters and amides and the reductive cleavages and C-C coupling reactions related with them.

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4 For instance representative Sm BDE's (kcal/mol) are as follows: Sm-Cl = 97(3), Sm-OR = 82(4), Sm-SR = 73(3) kcal/mol.

5 Ionic radii for eight coordinate complexes: Y^{3+} = 1.16 Å, La^{3+} = 1.30 Å, Ce^{3+} = 1.28 Å. See Shannon, R.D. *Acta Crystallogr.* **1976**, *A32*, 751.

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Chapter 2

C-H Activation of Arenes by the Yttrium Hydride $(Cp^*_2YH)_2$: Competition between Cp^* Ligand Metallation, Arene Metallation and H/D Exchange

Introduction

The 14 electron group 3 and lanthanide compounds Cp^*_2LnR ($Cp^* = \eta^5\text{-}C_5Me_5$, R = H, alkyl) are strong Lewis acids[1] which, in the absence of Lewis bases, even may attack the electron density of C-H bonds, thus forming agostic interactions[2] and activating these bonds.[1b,3] During our work on hydrocarbyl and hydride compounds Cp^*_2LnR and $(Cp^*_2LnH)_2$ with Ln = Y, La, Ce, we studied the activation of C-H bonds and observed that the crowded metal alkyls $Cp^*_2LnCH(SiMe_3)_2$, though much less reactive, show a reactivity very related to that of the hydrides $(Cp^*_2LnH)_2$. The yttrium compound $(Cp^*_2YH)_2$ (**1**) appeared to be the most reactive of the series and therefore we focused on this compound. Its reactivity in solvents like alkanes, benzene and toluene and its reactions with halobenzenes were studied to determine the selectivity of C-H activation and possible competition between C-H and C-X activation with this type of compounds. The results are described below.

Results and Discussion

Competition between C-H Activation of a Cp^* Ligand and C-H activation in Benzene and Toluene. Thermolysis of **1** in *n*-octane, cyclohexane or benzene leads to the internally metallated complex $Cp^*_2Y(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)YCp^*$ (**2**)[4] (eq 1). This reaction occurs in closed vessels but also when the hydrogen evolved is removed slowly. Binuclear complex **2** contains bridging hydride and tetramethylfulvene (Fv = $CH_2C_5Me_4$) ligands, the latter formed via hydrogen

abstraction from a Cp* ligand. A similar observation has been made for the analogous samarium hydride $(Cp^*_2SmH)_2$,[5] which emphasizes the strong resemblance of **1** and lanthanide hydrides.[1b] The formation of **2** is reversible and in closed systems a solution of **1**, although it contains in part **2**, reacts as if it were the intact dimeric hydride.

$$\underset{\mathbf{1}}{(Cp^*_2YH)_2} \rightleftharpoons \underset{\mathbf{2}}{Cp^*_2Y(\mu\text{-}H)(\mu\text{-}\eta^1;\eta^5\text{-}CH_2C_5Me_4)YCp^*} + H_2 \qquad (1)$$

In aromatic solvents a second C-H activation process is observed. When **1** is dissolved in deuterated benzene or toluene at room temperature, H/D scrambling between hydride ligands and solvent takes place at a rate too fast to follow experimentally, leading to formation of the deuteride $(Cp^*_2YD)_2$ and it is impossible to observe hydride resonances in the ^{1}H-NMR spectrum.[6,7]

The H/D exchange with benzene and toluene was monitored with ^{1}H-NMR spectroscopy by adding stoichiometric quantities of benzene-d_6 or toluene-d_8 to cyclohexane-d_{12} solutions of **1**. The loss of hydride intensity was attended by a matching increase in intensity of the benzene and toluene resonances respectively. Superimposed on this scrambling reaction is the thermolysis to **2**. With toluene-d_8, after 26 h at room temperature, 20 % of the hydride ligands of **1** were still present and 30 % had been exchanged for deuteride ligands. The remaining 50 % of **1** had been converted to **2**. The intensity ratio H(*para*) : H(*meta*) : H(*ortho*) : H(methyl) = 1.1 : 2.3 : 1.1 : 1.0 was observed, indicating a clear preference for H/D scrambling on the *para* and *meta* positions. These observations are in close agreement with the corresponding scandium system.[8]

These results indicate that **1** is an efficient catalyst for the activation of C-D/C-H bonds in aromatic hydrocarbons. For non-deuterated aromatic hydrocarbons this is not a productive process however. In contrast to deuterated benzene and toluene, the sp^3 C-H bonds of cyclohexane-d_{12} are not susceptible to H/D exchange and no significant H/D exchange was observed during the thermolysis of **1** in this solvent (several days at room temperature).

In addition to fast H/D exchange and the slow intramolecular C-H activation which gives **2**, a third reaction was observed which, at an intermediate rate, leads to metallation of solvent molecules under formation of hydrogen (eq 2). This C-H activation competes with Cp*-metallation and compounds Cp^*_2YR (R = Ph (**3**),

$PhCH_2$ (4)) can be trapped as the kinetic products when the hydrogen is removed sufficiently rapidly.

$$(Cp^*_2YH)_2 + 2\,RH \rightleftharpoons Cp^*_2YR + 2\,H_2 \qquad (2)$$

1 — **3**, R = Ph; **4**, R = CH_2Ph

The method is not clean, as small amounts of the bridged hydride fulvene **2** are obtained as well. For benzene this leads to a 6 : 1 mixture of **3** and **2**. Toluene is metallated faster, resulting in a 11 : 1 ratio of **4** and **2**. It is clear from competition experiments that **2** is the thermodynamic product, obtained when thermolysis of **1** is carried out slowly, i.e. when hydrogen is removed gradually during a couple of days at room temperature. Eq 2 is positioned strongly on the side of the starting material **1** and in closed NMR tubes less than 1 % of **1** is converted to metallation products.

In principle, H/D scrambling could take place via metallation (Scheme I). After dissociation of 1,[9] an arene molecule is metallated with formation of HD. The new Y-C bond can be hydrogenolyzed in the second step by HD to give Cp^*_2YD and protonated solvent. Another possibility is that after dissociation of **1**, H/D scrambling involves the direct exchange of a proton for a deuteron between monomeric hydride and solvent. The fact that H/D scrambling between **1** and toluene-d_8 takes place dominantly at the aryl C-H positions while only the benzyl **4** can be obtained under dynamic vacuum, suggests that the pathway for H/D (H/H) exchange is different from that of metallation, because otherwise a mixture of yttrium tolyls $Cp^*_2YC_6H_4Me$ and the benzyl **4** is expected.

Scheme I

$$Cp^*_2YH + RD \rightleftharpoons Cp^*_2YR + HD$$

$$Cp^*_2YR + HD \rightleftharpoons Cp^*_2YD + RH$$

The observation that H/D scrambling between H_2 (4 atm) and toluene-d_8 in the presence of **1** is slow, whereas in the same experiment scrambling between **1** and toluene-d_8 is fast, indicates that H_2, D_2 and HD are not intermediates in the latter

process. Ring metallation of toluene is therefore probably not on the reaction coordinate for H/D scrambling between **1** and solvent.

One way to account for the different observations within the framework of the well known σ-bond metathesis mechanism[3] is that there are two possibilities for the incoming molecule RH to form a transition state. The most easily achieved considering steric interactions upon approach of molecule RH is situation A (Figure 1), with R symmetrically positioned between two hydrogen atoms, leading to non-productive metathesis when hydrogen atoms are involved and to catalytic H/D scrambling when deuterated substrates R-D are introduced. Situation B is the transition state normally anticipated and leads to a metallated species and H_2 (or HD). So far, transition state A has hardly been mentioned as a possibility in early transition metal chemistry and theoretical analyses,[10] but it has been proposed to explain H/D exchange between benzene-d_6 and R_3SiH by the d^2 system Cp^*_2NbH.[11] Despite the fact that the transition state in the latter system is assumed to correspond to an oxidative addition of C-D respectively Si-H to a Nb(III) center, we believe that the steric aspects of the two systems are directly comparable.

The reactions with benzene and toluene show that **1** behaves very much like the Sc, Lu and other lanthanide analogues. Both $(Cp^*_2ScH)_2$[8] and $(Cp^*_2LuH)_2$[12] give facile H/D scrambling between the hydride ligands and deuterated benzene or toluene. They also form phenyl complexes when H_2 is purged from the reaction mixture. Metallation of toluene to form the benzyl $Cp^*_2MCH_2Ph$ has also been observed for the cerium alkyl $Cp^*_2CeCH(SiMe_3)_2$[13] and for the dimeric samarium hydride $(Cp^*_2SmH)_2$.[5]

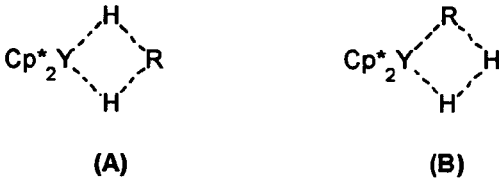

Figure 1. Transition states in non-productive (A) and productive (B) σ-bond metathesis.

The formation of hydride fulvene complexes $Cp^*_2M(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)MCp^*$ has not been reported for M = Sc and Lu, although these systems have been studied under conditions comparable to those under which we

studied the thermolyses of 1 Bercaw *et al.*[8] observed that, in aliphatic hydrocarbon solvents and under reduced hydrogen pressures, $(Cp^*_2ScH)_2$ decomposes but the nature of the product(s) was not established. In the light of our results it seems likely that also for scandium the formation of a fulvene hydride $Cp^*_2Sc(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)ScCp^*$ can take place when other possibilities are blocked. Evans *et al.*[5] observed the formation of an analogous hydride fulvene complex from $(Cp^*_2SmH)_2$ in alkanes and benzene i. e. under conditions close to those described by us for yttrium. These authors do not mention a transient side product Cp^*_2SmPh, but in toluene they observe formation of a mixture of $Cp^*_2Sm(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)SmCp^*$ and the benzyl $Cp^*_2SmCH_2Ph$, which strongly suggests that the various C-H activation processes take place at samarium and therefore at other analogous lanthanide centers as well. The main difference will be the relative rates, which will determine the kinetic products, but also the thermodynamics may vary from metal to metal leading to variations in final product composition, although the differences probably will be marginal.

A prerequisite for high H/D scrambling and metallation activity seems to be the presence of a terminal hydride ligand.[5,9,14] For $(Cp^*_2LnH)_2$ complexes with small metal centers (Ln = Sc, Lu, Y) this is realized by dissociation of the dimeric hydride in solution. The similarities in behaviour of 1 and the scandium and lutetium analogues suggest that dissociation is at least kinetically within range. These considerations can also explain why the bridging hydride ligand in 2 does not undergo H/D exchange with benzene-d_6 (18 h, room temperature) since breaking up of the hydride bridge is expected to be more difficult here.

The observations discussed above illustrate how subtle differences in experimental conditions can drastically influence the ultimate products from C-H activation reactions of 1. This is caused by the small differences in kinetics of the various C-H activation routes available. It is evident that 1 and the species derived from it through thermolysis and solvent metallation are very reactive. Their role should be taken into account when reactions of 1 with other substrates are studied.

Metallation of Substituted Arenes PhX. We were interested to see whether the presence of a substituent X in the substrate molecule would influence the selectivity of the C-H activation and especially whether activation of group X would compete. Therefore we studied the reaction of 1 with substituted aromatic compounds PhX (X = F, Cl, Br). From organolithium chemistry it is known that several substituents on

the aryl ring can function as an ortho-directing group, e. g. -OMe, -NMe_2, and -CH_2NMe_2.[15]

The reaction of **1** with PhX (X = F, Cl, Br) in cyclohexane-d_{12} was instantaneous but a complicated mixture of yet unidentified compounds was formed. Formation of benzyne was indicated from GC/MS analysis after quenching the fluorobenzene reaction mixture with water. In addition to a significant amount of 2-fluorobiphenyl, three other major components were observed which, according to the molecular mass, were provisionally identified as resulting from attack of benzyne on Cp* ligands. Due to the complexity of the reaction and the resulting hydrolysis mixture, a detailed investigation of these systems was not pursued. However, in a preparative reaction of **1** with fluorobenzene, a biphenyl derivative $Cp^*_2Y(2\text{-}C_6H_4\text{-}C_6H_4F)$ (^{1}H-NMR) was isolated in low yield (6 %). This indicates that C-X bonds are activated, possibly after initial *ortho*-metallation of fluorobenzene. C-C coupling can then take place either by attack of benzyne on a Cp* ligand, or by insertion into the Y-C bond of the initial metallation product $Cp^*_2Y(2\text{-}C_6H_4F)$. Since the ^{1}H-NMR spectra of the chloro- and bromobenzene reactions with **1** are very similar to that obtained with fluorobenzene, these benzene derivatives are assumed to react analogously.

Concluding Remarks

The yttrium hydride $(Cp^*_2YH)_2$ (**1**) very easily enters various C-H activation processes and, in addition to non-productive H/H (H/D) exchange, competition between intramolecular activation of a pentamethylcyclopentadienyl ligand and intermolecular attack of aromatic solvents is observed. For most possibilities the activation barriers are comparable, thus leading to mixtures of kinetic products. Also the differences in free energies between the various products appear not to be very pronounced, so that frequently complicated equilibria result and separation of the various components is virtually impossible. In relatively inert solvents (alkanes) the dominant product is the fulvene hydride $Cp^*_2Y(\mu\text{-}H)(\mu\text{-}\eta^1;\eta^5\text{-}CH_2C_5Me_4)YCp^*$ (**2**), formed by extrusion of H_2 through activation of a methyl group on one of the pentamethylcyclopentadienyl ligands of the dimeric hydride.

In deuterated aromatic solvents fast H/D exchange between the hydride ligand and all solvent positions takes place indicating a low activation energy pathway for this, in general terms, non-productive σ-bond metathesis. This high H/D scrambling

activity seems to be related to the facile dissociation of **1** into reactive monomers. The metallation of benzene, toluene and PhX as well as the intramolecular sp^3 C-H activation of the methyl group of a Cp* ligand to give the fulvene hydride **2** follows another pathway. With benzene and toluene the kinetic products are the phenyl complex Cp^*_2YPh (**3**) and the benzyl $Cp^*_2YCH_2Ph$ (**4**), respectively. With PhX substrates with X = F, Cl, Br there were indications for activation of C-X bonds after initial metallation.

Experimental Section

General Considerations. All experiments were performed under nitrogen using standard Schlenk, glovebox (Braun MB200), and vacuum line techniques. Benzene, toluene, pentane, cyclohexane, benzene-d_6, toluene-d_8 and THF-d_8 were distilled from Na/K alloy and degassed prior to use. **1** was prepared according to a published procedure.[7] Hydrogen (Hoek-Loos, 99.9995 %) was used without further purification. Other reagents, cyclohexane-d_{12} and methylcyclohexane-d_{14} were stored over mol sieves (4 Å) and degassed prior to use. NMR spectra were recorded on Gemini 200 (^{1}H: 200 MHz) and Varian VXR-300 (^{1}H: 300 Mhz, ^{13}C: 75.4 MHz) spectrometers at ambient temperatures. GC/MS analyses (EI) were carried out on a Ribermag R 10-10 C instrument using a CP Sil 5 CB column.

H/D Scrambling Reactions of $(Cp^*_2YH)_2$ (1) with Benzene and Toluene. 12 mg (0.017 mmol) of **1** was dissolved in 0.5 mL of benzene-d_6. Within 5 minutes volatiles were removed in vacuum and the residu was dissolved in 0.5 mL of cyclohexane-d_{12}. When the ^{1}H-NMR spectrum of this solution was compared to that of **1** in cyclohexane-d_{12} the hydride resonances turned out to be absent. The C_5Me_5 resonance however was observed at the same chemical shift.

H/D scrambling reactions were followed by monitoring solutions of 0.037 mmol of benzene-d_6 or toluene-d_8 and 13.2 mg (0.018 mmol) of **1** in 0.6 mL of cyclohexane-d_{12} with ^{1}H-NMR spectroscopy at room temperature. For toluene the volatiles were pumped off after 26 h and from the ^{1}H-NMR spectrum the ratio of proton incorporation into the different positions of toluene was established. To investigate the H/D scrambling between H_2 and toluene-d_8 by **1**, an NMR tube containing 17 mg (0.024 mmol) of **1** in 0.61 mL (5.6 mmol) of toluene-d_8 was sealed under 4 atm (0.3 mmol) of H_2. The increase in the integration of the aryl

resonances of the solvent was monitored by ^{1}H-NMR spectroscopy at regular intervals during 5 d at room temperature. The methyl resonance of toluene was not observed due to overlap with the C_5Me_5 resonance of **1**. Immediately after preparation of the NMR tube the intensity of the aryl-hydrogen signals of toluene corresponded to 0.05 mmol of hydrogen atoms and the hydride signal was absent. After 30 min the intensity of the aryl-hydrogen signals of toluene corresponded to 0.088 mmol hydrogen atoms. After 68 h at room temperature this value had increased to 0.17 mmol.

Metallation of Benzene by 1. 15 mg (0.021 mmol) of **1** was dissolved in 20 mL of benzene and stirred for 4 h under dynamic vacuum at room temperature. Volatiles were removed under vacuum and the ^{1}H-NMR spectrum of the remaining oil in cyclohexane-d_{12} indicated that a mixture of 68 % of **3**, 11 % of **2** and some unidentified material had been formed. ^{1}H-NMR of **3** (300 MHz, cyclohexane-d_{12}): δ 7.08 (t, $^3J_{HH}$ = 7 Hz, 2H, *meta* H's), 6.98 (t, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz, 1H, *para* H), 6.72 (dd, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 1 Hz, 2H, *ortho* H's), 1.78 (s, 30 H, C_5Me_5).

Metallation of Toluene by 1. A stirred solution of 50 mg (0.069 mmol) of **1** in 2.5 mL of toluene was evaporated to dryness in 1/2 h at room temperature. The yellow oil which remained was dissolved in cyclohexane-d_{12} and the ^{1}H-NMR spectrum indicated that a mixture of 80 % of **4**, 13 % of unreacted **1** and 7 % of **2** had been formed. ^{1}H-NMR of **4** (200 MHz, cyclohexane-d_{12}): δ 6.92 (t, $^3J_{HH}$ = 7.3 Hz, 2H, *meta* H's), 6.63 ($^3J_{HH}$ = 6.8 Hz, 1H, *para* H), 6.53 (d, $^3J_{HH}$ = 7.3 Hz, 2H, *ortho* H's), 1.91 (d, $^1J_{YH}$ = 6.0 Hz, 2H, YCH_2), 1.83 (s, 30H, C_5Me_5).

NMR and GC/MS Analysis of the Reaction of 1 with Fluorobenzene. 8.8 μL (0.093 mmol) of fluorobenzene was added to a suspension of 34 mg (0.047 mmol) of **1** in 0.5 mL of cyclohexane-d_{12}. Immediately gas evolution was observed and **1** dissolved completely. 1H-NMR spectroscopy indicated that **1** had been converted to a complicated mixture of unidentified products. The NMR tube was opened and 1.5 mL of cyclohexane and 6 μL of water were added. After filtration over a column of $MgSO_4$ the mixture was analyzed by GC/MS. In addition to 2-fluorobiphenyl, three compounds with M^+ peaks at m/z = 212 were present.

Preparative Scale Reaction of 1 with Fluorobenzene. A suspension of 1.09 g (1.51 mmol) of 1 in 40 mL of pentane was cooled to -70 °C and 284 μL (3.03 mmol) of fluorobenzene was added. The reaction mixture was allowed to warm to room temperature in 30 min during which gas evolution was observed and 1 dissolved completely. Volatiles were removed in vacuum and the remaining oil gave a cream-colored precipitate after washing with 2.5 mL of pentane. Crystallisation from 25 mL pentane at -80 °C gave 0.100 g of cream-colored crystals (0.19 mmol, 6 %). ^{1}H-NMR (200 MHz, benzene-d_6): δ 7.77-7.66 (m, 2H, aryl H), 7.33-7.24 (m, 2H, aryl H), 6.94-6.57 (m, 3H, aryl H), 1.83 (s, 30H, C_5Me_5), an additional aryl signal overlapped with the solvent signal.

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6 In contrast to what was published earlier by our group,[7] the ^{1}H-NMR data (300 MHz, methylcyclohexane-d_{14}, 300 K) for 1 are as follows: δ 5.45 (broad s, 2H, Y-H-Y), 2.06 (s, 60 H, C_5Me_5). Heating the solution to 355 K did lead to a slightly sharpened hydride resonance, the high temperature limit could however not be reached due to severe thermal decomposition of the compound. On cooling, the broad singlet hydride resonance splits into a triplet ($^1J_{HY}$ = 37.5 Hz) already at 288 K. Subsequent cooling to 195 K does not lead to further substantial changes of the NMR spectrum. This implicates that below room temperature 1 exists as a dimer with symmetrically bridging hydride ligands.

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Chapter 3

A Theoretical Study on C-H Activation Reactions by Organo-Lanthanide Hydride Complexes; H/D Scrambling vs Metallation of Hydrocarbons

Introduction

In our work on organo-yttrium compounds[1] we have found indications for an alternative sigma-bond metathesis mechanism, leading to H/D scrambling between an yttrium hydride complex and deuterated arenes (eq 1). Also the more common sigma-bond metathetical metallation of arenes was observed (eq 2). The two types of C-H activation lead to activation of different C-H bonds. For toluene, H/D scrambling took place mainly at the aryl positions while in the metallation reaction only the benzylic position was attacked giving $Cp^*_2YCH_2Ph$. A mechanism involving the direct (concerted) transfer of a hydrogen for a deuterium atom was proposed to explain these observations. Such a process would involve transition state **1** (Figure 1) in which the aryl group is positioned on the C_2 axis of the Cp_2M fragment.

$$(Cp^*_2YH)_2 + 2\,RD \rightarrow (Cp^*_2YD)_2 + 2\,RH \qquad (1)$$

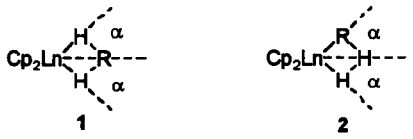
$$(Cp^*_2YH)_2 + 2\,RH \rightarrow 2\,Cp^*_2YR + 2\,H_2 \qquad (2)$$
$$R = Ph,\ CH_2Ph$$

$$L_nMR + R'H \rightarrow L_nMR' + RH \qquad (3)$$
$$R = H \text{ or hydrocarbyl}$$

Normally, C-H activation of hydrocarbons by early transition metal and f-element complexes (eq 3) involves a four-centered transition state **3** (Figure 2). For

This work has been performed in collaboration with O. Eisenstein and S.A. Macgregor from the Université de Paris-Sud in Orsay.

these complexes, oxidative addition of a C-H bond on the metal center is not possible since the metal center has usually a d^0 configuration preventing the electrophilic metal to change its formal oxidation state. C-H activation reactions of this type have been studied for Sc and Lu by Bercaw[2] and Watson[3] *et al.*, respectively.



1 2

Figure 1. Proposed four-centered transition states in C-H activation of RH by $(Cp^*_2LnH)_2$ complexes (Ln = Sc, Y, Lu).

Sigma-bond metathesis reactions of the type of eq 3 are mechanistically addressed by several theoretical approaches. One of the first is the ab initio (GVB) study by Steigerwald and Goddard on the reactions of D_2 with titanium and scandium hydrides.[4] For Cp_2Lu complexes extended Hückel calculations have been carried out by Hoffmann *et al.*[5] A paper by Rappé deals with sigma-bond metathesis reactions of acetylene with Cl_2ScH.[6] More recently a very elaborate investigation on scandium complexes, based on density functional theory, has been reported by Ziegler and co-workers.[7] The proposed four-centered transition states involved are of type **3**. It has been pointed out by several authors that the central position of this transition state is not well suited to accommodate an alkyl group since the sp^3 hybrid orbital involved doesn't give good overlap with orbitals on the other centers in the cyclic transition state.[2,7]

3

Figure 2. Four-centered transition state in C-H activation by early transition metal and f-element complexes leading to metallation of R'H.

Our results for Y are similar to those obtained for corresponding Sc and Lu complexes, but a different sigma-bond metathesis mechanism was not proposed for

these metals however. A transition state analogous to **1** was discarded in the H/D scrambling between acetylene and Cl_2ScH because of the high activation barrier.[6] For other hydrocarbons the activation energy is not known however. Therefore we decided to perform a theoretical study on the transition states **1** and **2** (Figure 1). We were especially interested in whether the H/D scrambling process via transition state **1** could compete with the metallation via transition state **2** for R = Ph. We performed extended Hückel MO calculations on models of both transition states and compared their total energies and orbital interactions. The transition states for C-H activation of methane were studied for comparison.

Results and Discussion

Because no reliable extended Hückel parameters are available for Y, we started off with calculations on the corresponding Lu complex since the chemistry of these metals is very related[1] and the f electrons are chemically insignificant.[5] For simplicity we used normal Cp ligands instead of pentamethylated Cp's. The first problem we faced was to construct reasonable transition states for the direct H/H exchange and the metallation reactions. For this purpose we used the strategy which Hoffmann *et al.* followed in their study on the methane exchange reaction with Cp_2LuMe.[5] Both the hydride ligands and the hydrocarbyl group of the HRH and RHH fragments were positioned in the plane between the Cp rings within bonding distances to the metal center (Figure 3). In all cases the angle α was kept fixed at 35°, which is a reasonable value when calculations on similar transition states are considered.[5,7]

H/H Exchange vs Metallation for Benzene. The transition state models used for the calculations on the benzene reactions are shown in Figure 3 (**4** and **5**). In both cases the phenyl group was rotated along the Ln-C bond. A clear preference for the conformation with the phenyl group oriented perpendicular to the plane between the Cp rings was found (*i.e.* $\beta = 90°$ with β being defined as the H1-Ln-C8-C9 torsion angle). For **5** this orientation was calculated to be favoured by 4.1 eV relative to the situation with $\beta = 0°$ (Figure 4). For transition state **4** there is a smaller preference of 0.9 eV for the orientation of the phenyl group perpendicular to the plane between the Cp rings.

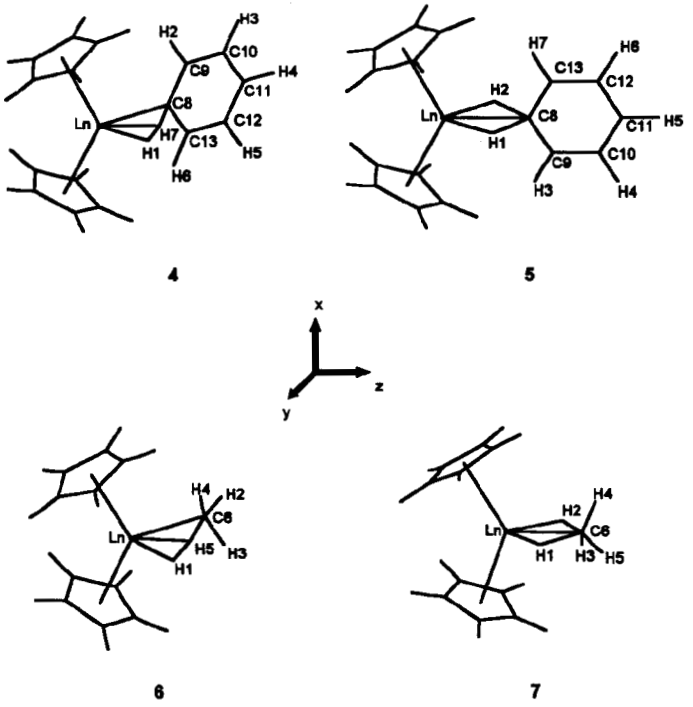


Figure 3. Transition state models used in calculations.

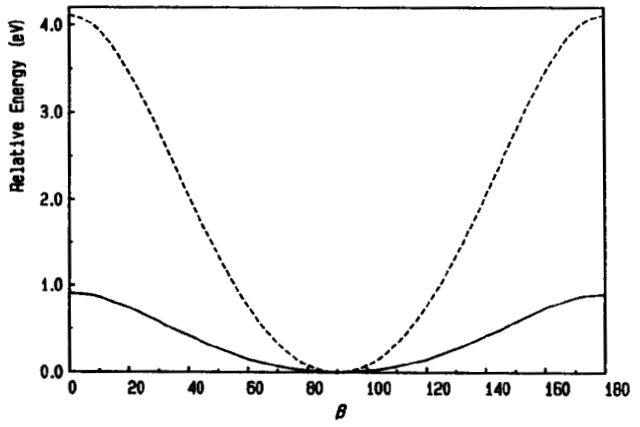


Figure 4. Dependence of the total energies of **4** (solid line) and **5** (dashed line) on rotation of the phenyl group along the Lu-C axis.

A fragment molecular orbital (FMO) analysis was performed for both models with the phenyl groups oriented in the energetically most favourable orientations (β = 90°). The MO picture of the $[Cp_2Lu]^+$ fragment is represented in Figure 5.[8] There are three high-lying frontier orbitals which are mainly metallic in character and are shown schematically. These orbitals are situated above the empty π*-block of the Cp ligands.

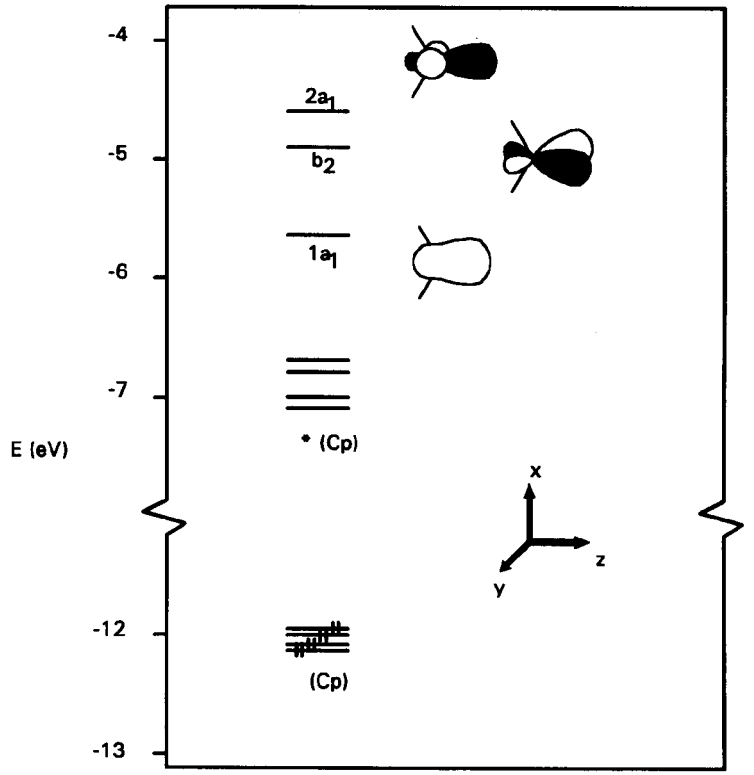


Figure 5. Frontier orbitals of the $[Cp^*_2Lu]^+$ fragment.

For Lu transition state **4**, leading to metallation, was treated as being composed of a $[Cp_2Lu]^+$ and a $[Ph\text{-}H\text{-}H]^-$ fragment (Figure 6, left side). For simplicity no rehybridization of C8 was allowed. Only FMO 16 of the $[Ph\text{-}H\text{-}H]^-$ fragment has significant bonding interaction with an orbital on the metal fragment (b_2). The resulting molecular orbital (MO 49) is significantly stabilized and situated at -11.80 eV. The FMO population analysis yields 1.74 and 0.27 electrons, respectively for

the contributing FMO's. For transition state **5** $[Cp_2Lu]^+$ was allowed to interact with $[H\text{-}Ph\text{-}H]^-$ resulting in a interaction diagram very similar to that of **4** (Figure 6, right side). Here again the in-phase combination of FMO 16 on $[H\text{-}Ph\text{-}H]^-$ and the b_2 orbital on $[Cp_2Lu]^+$, is the single bonding interaction between the two fragments. Also the FMO population analysis for the contributing FMO's, 1.78 and 0.25 electrons, respectively, is very similar to that of transition state **4**. The resulting molecular orbital MO 49 at -11.38 eV lies at slightly higher energy relative to the corresponding orbital in **4** (-11.80 eV). As a result of these small energy differences, the total energies of **4** and **5** are almost comparable with **4** being only 0.36 eV more stable than **5**.

When reorientation of the phenyl group is allowed by varying the angle χ (Figure 7), a minimum is found at $\chi = 30°$ leading to a stabilization of -0.27 eV of **4**. This is caused by better overlap within the $[Ph\text{-}H\text{-}H]^-$ fragment which results in the lower energy of FMO 16. For **5** there is no tendency for reorientation of the phenyl group. As a result of this reorientation, **4** is now favored over **5** by 0.63 eV.

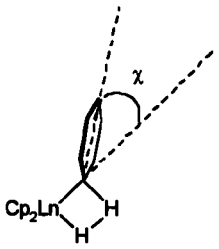


Figure 7. Reorientation of the phenyl group in **4**.

Since extended Hückel parameters are not yet reported for Y, an accurate study is not possible for Ln = Y. However, making an estimate of the parameters allowed us to study the parameter dependence of the calculations and to make some statements about the C-H activation reactions for Y. The Zr parameters were used to approximate the s and p levels of Y. The d levels of Y were estimated by taking $H_{ii} = -10.5$ eV and using the Slater coefficients and exponents of Zr, assuming that the spatial extensions of these levels are comparable. The geometry was kept the same as for Ln = Lu.

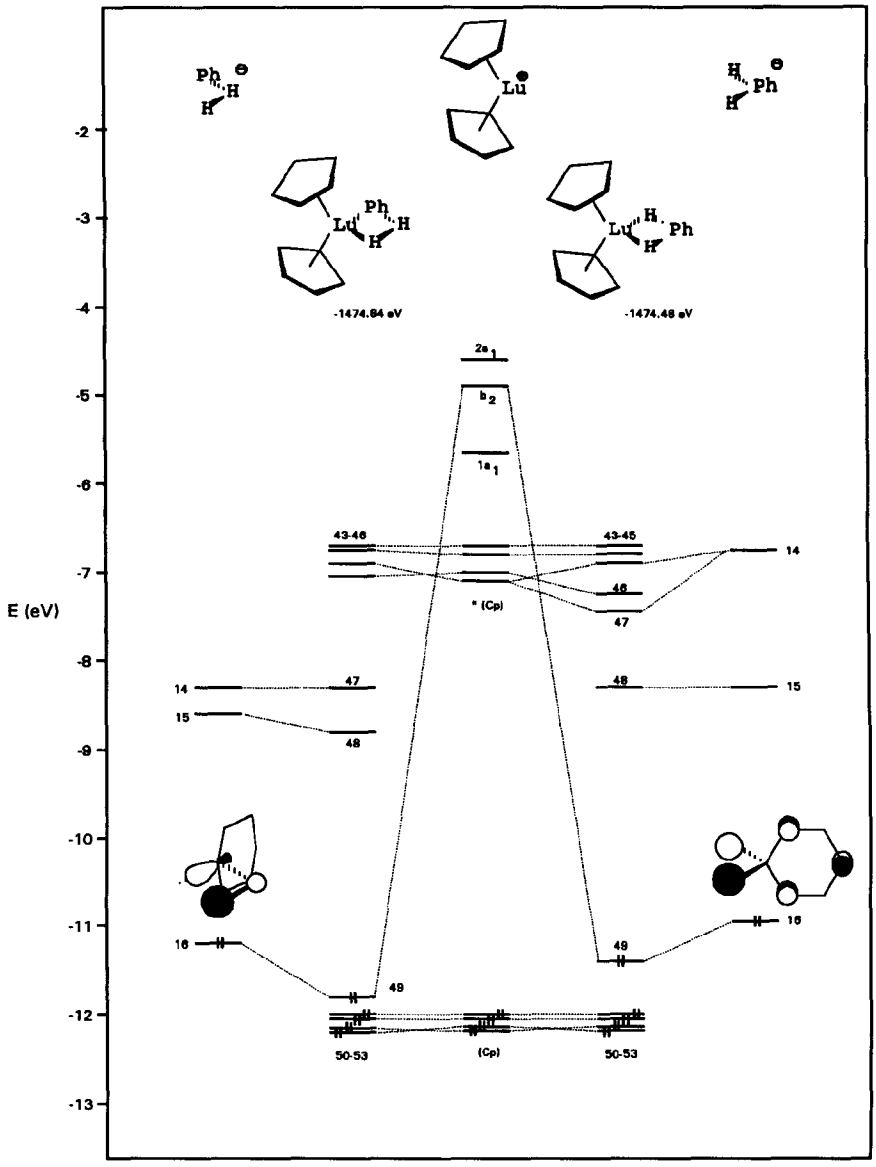


Figure 6. Interaction diagram for **4** (left side) and **5** (right side).

The difference in total energies of **4** and **5** using these parameters is identical to that using the Lu parameters (without reorientation of the phenyl group). Again **4** is

favored by 0.36 eV over **5** and as was found for Lu, the major interaction is that of the b_2 orbital of the $[Cp_2Ln]^+$ fragment and the HOMO of the [Ph-H-H]$^-$ and the [H-Ph-H]$^-$ fragments respectively. The overlap populations are higher however, due to the smaller energy differences between the FMO's. These results indicate that the energy of the frontier orbitals of the metal fragment has little effect on the energy difference between the transition states for metallation and H/H exchange and should therefore be relatively insensitive to variations in Ln.

H/H Exchange vs Metallation for Methane. For methane, the energies of the transition state models **6** and **7** didn't change much with rotation of the methyl group along the Ln-C bond (Figure 8). The lowest energy conformations were used in the calculations with $\beta = 180°$ (β being defined as the H1-Ln-C6-H4 (**6**) and H2-Ln-C6-H3 (**7**) torsion angles respectively). Since the potential energy curves are very shallow, other conformations of the methyl group are very well possible however. In both cases no rehybridization of the methyl group was allowed for simplicity.

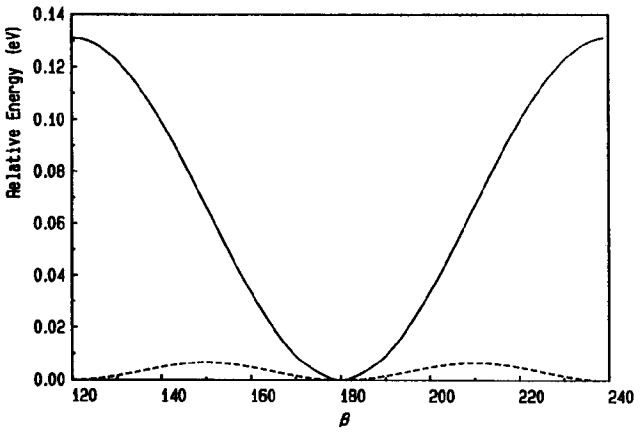


Figure 8. Dependence of the total energies of **6** (solid line) and **7** (dashed line) on rotation of the methyl group along the Lu-C axis.

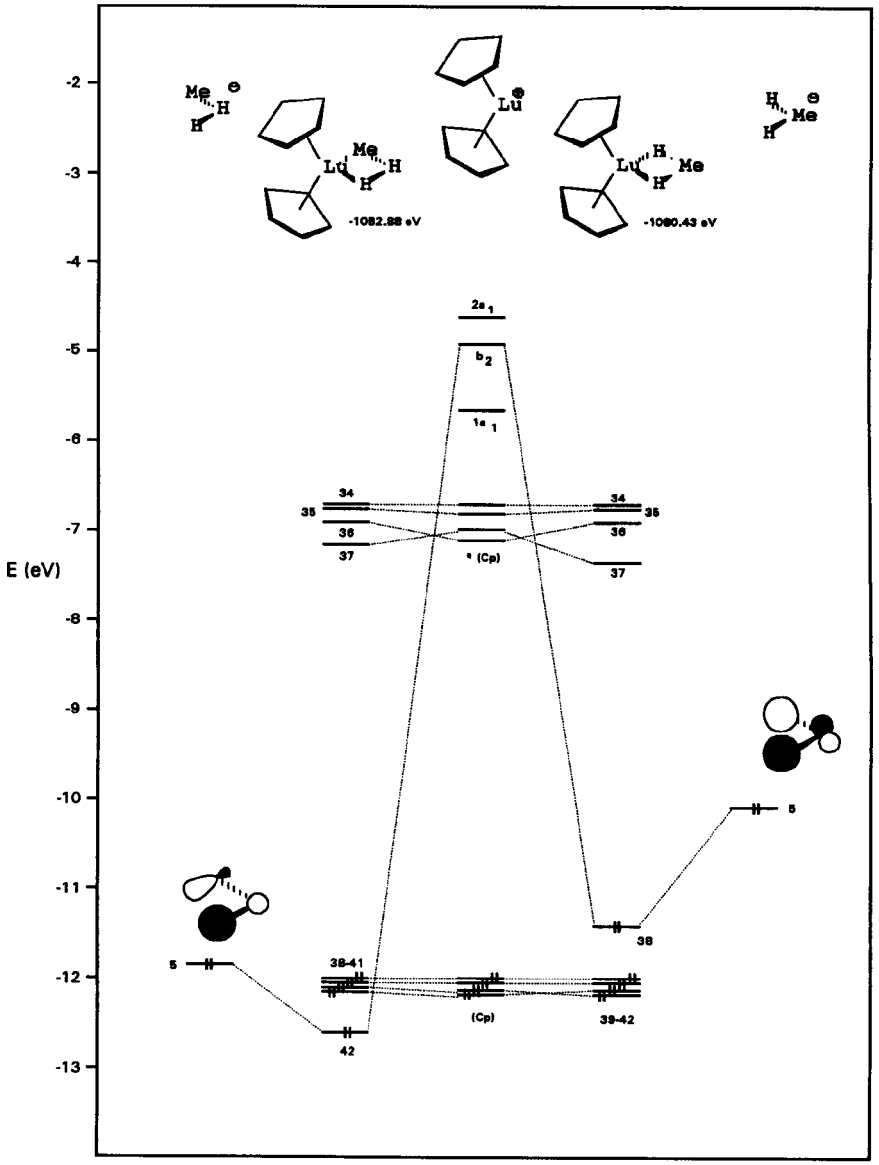


Figure 9. Interaction diagram for **6** (left side) and **7** (right side).

The interaction diagram resulting from the FMO analysis of **6** and **7** is presented in Figure 9. Again we see only one important bonding interaction. For **6** this is

FMO 5 of the [Me-H-H]$^-$ fragment which interacts effectively with the b_2 level on the metal fragment resulting in MO 42 situated at -12.61 eV, even below the π-block of the Cp ligands. The FMO population analysis yields 1.71 and 0.26 electrons for the contributing FMO's, respectively. For **7** it is again FMO 5 of the [H-MeH]$^-$ ligand which interacts with FMO 28 of the metal fragment. The FMO population analysis gives 1.55 and 0.38 electrons, respectively. Although this interaction is clearly stronger as for the [Me-H-H]$^-$ fragment, the resulting MO 38 lies still 1.22 eV higher in energy at -11.39 eV, because FMO 5 lies at much higher energy compared to the corresponding level of the [Me-H-H]$^-$ fragment. The difference in energy of the resulting MO's is almost completely responsible for the 2.45 eV difference in total energy of **6** and **7**.

Analysis of the Bonding Situation in [R-H-H]$^-$ and [H-R-H]$^-$ Fragments. As is evident from the MO diagrams of Figures 6 and 9, the energy differences of the transition states for metallation and H/H exchange are mainly caused by the different bonding situation in the [R-H-H]$^-$ and [H-R-H]$^-$ fragments and to a lesser extent by the interaction with the $Cp^*_2Ln^+$ fragment. For methane the large energy difference between **6** and **7** is mainly due to the energy difference of the HOMO's of the [Me-H-H]$^-$ and [H-Me-H]$^-$ fragments (-11.84 and -10.18 eV respectively). For benzene the difference in energy of the HOMO's of the [Ph-H-H]$^-$ and the [H-Ph-H]$^-$ fragments is much less (-11.22 and -10.95 eV respectively) resulting in the comparable energies of **4** and **5**. To be able to pinpoint the deciding factor causing these differences in HOMO energies, we analyzed the interaction in the [R-H-H]$^-$ and [H-R-H]$^-$ fragments themselves.

Therefore [R-H-H]$^-$ and [H-R-H]$^-$ were split into [R]$^-$ and [HH] parts while keeping the same geometry as for the transition state models. The resulting energy level diagrams are depicted in Figures 10 and 11. For methane (Figure 10) the HOMO of [H-Me-H]$^-$ consists of the antibonding combination of the π-orbital of the Me group with the antibonding combination of the two hydrogen orbitals which is a destabilizing effect. For [Me-H-H]$^-$ such a destabilizing interaction is absent and the HOMO consists of a bonding interaction of the Me σ-orbital with the antibonding combination of the hydrogen orbitals. It is the strongly destabilizing interaction of the Me π_y-orbital with the [HH] fragment which is responsible for the higher energy of the [H-Me-H]$^-$ fragment compared to that of [Me-H-H]$^-$ (-164.04 and -167.76 eV respectively).

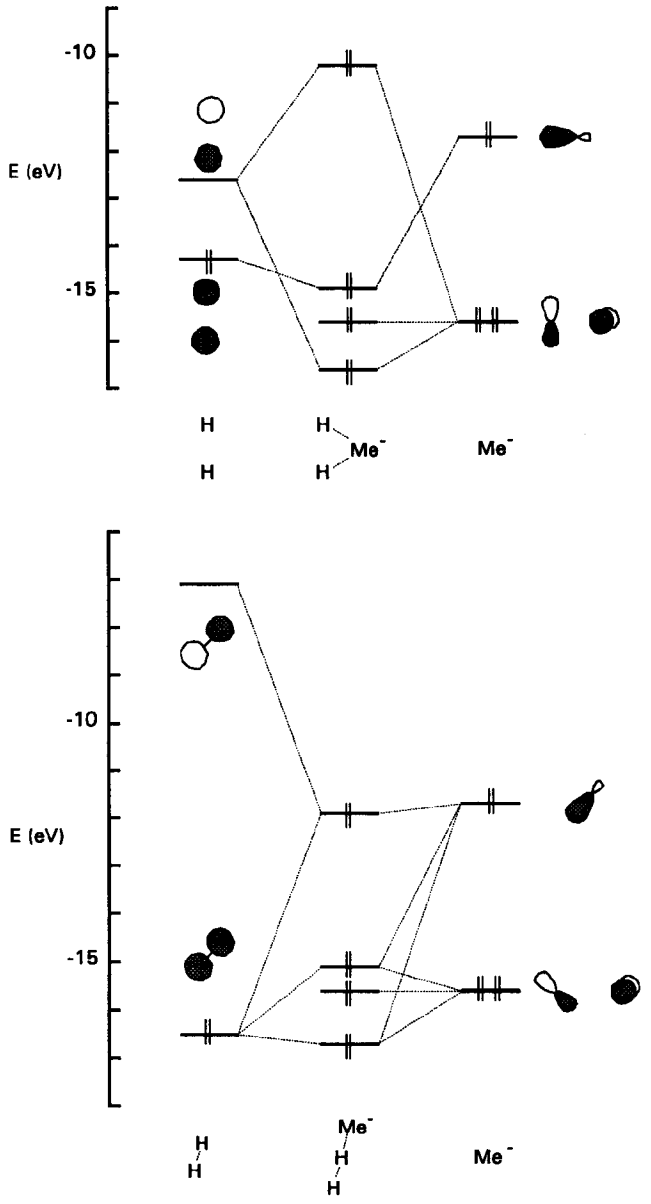


Figure 10. Interaction diagram for $[H\text{-}Me\text{-}H]^-$ fragment in transition state for H/H exchange (top) and for $[Me\text{-}H\text{-}H]^-$ fragment in transition state for metallation (bottom).

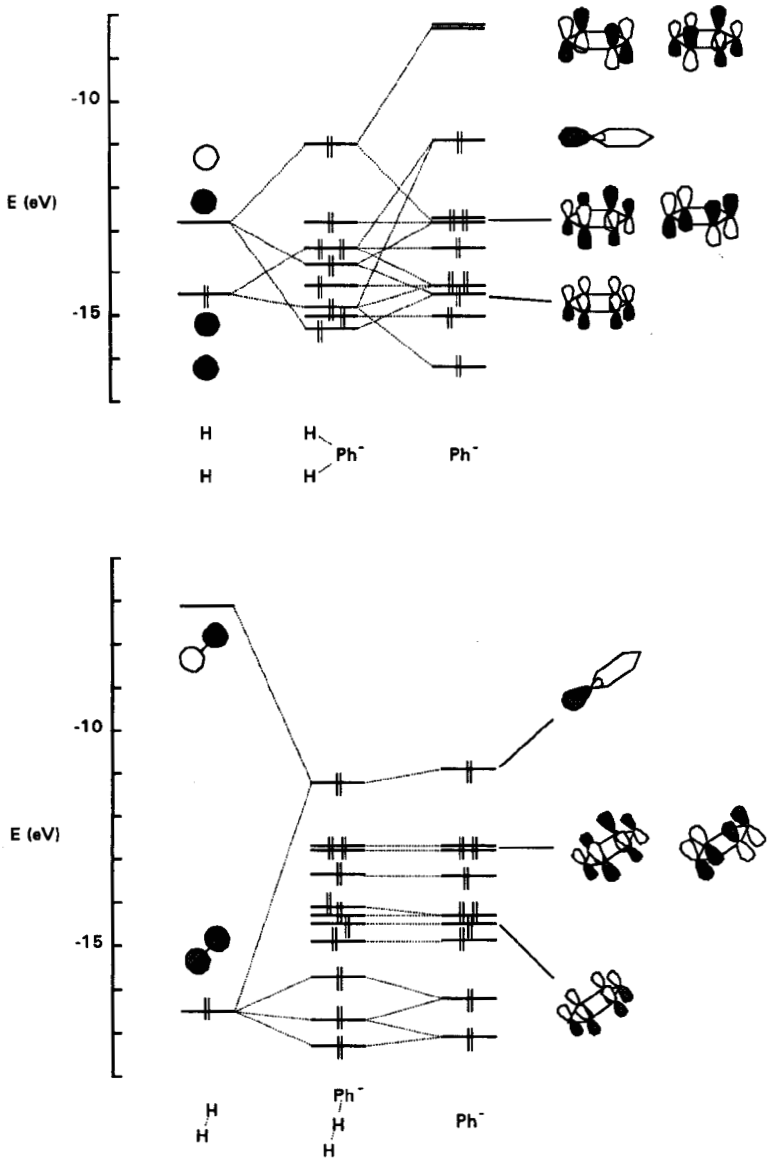


Figure 11. Interaction diagram for [H-Ph-H]⁻ fragment in transition state for H/H exchange (top) and for [Ph-H-H]⁻ fragment in transition state for metallation (bottom).

For benzene the picture is totally different (Figure 11). In the H/H exchange case there is also a destabilizing interaction from the π-system of the phenyl group but this is compensated by a stabilizing interaction with the low lying π*-levels of the phenyl which results in a relatively low lying HOMO. The bonding situation in [Ph-H-H]$^-$ on the other hand is very similar to the corresponding [Me-H-H]$^-$ fragment. Here the HOMO is mainly a bonding combination of the σ-orbital of the phenyl group with the antibonding combination of the hydrogen orbitals. The interaction with the π-system of the phenyl group is insignificant here. The result is that [H-Ph-H]$^-$ and [Ph-H-H]$^-$ are much closer in energy (-559.50 and -559.53 eV respectively) than are [H-Me-H]$^-$ and [Me-H-H]$^-$.

The overlap of the hydride orbitals with the phenyl π-system can be visualized as a nucleophilic attack of H$^-$ on benzene resulting in the delocalization of the negative charge over the ring positions (Figure 12). For methane this is not possible due to the absence of a low lying π*-orbital. Also in the transition state for metallation of benzene the stabilizing interaction with the π-system of benzene cannot be achieved. The overall result is that for benzene the H/H exchange reaction is favored relative to metallation, whereas for methane metallation is more facile than H/H exchange.

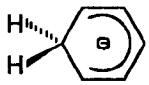


Figure 12. Nucleophilic attack of H$^-$ on benzene.

Comparison with Experimental Observations. As a result of the stronger bonding in the [Me-H-H]$^-$ fragment vs the [H-Me-H]$^-$ fragment we would expect that for methane metallation is more facile than H/H (H/D) exchange, whereas for benzene the rate of the two processes should be comparable. For benzene H/H (H/D) exchange is expected to compete effectively with metallation since transition state **4** and **5** are of similar energy. Indeed this corresponds qualitatively with experimental observations.[1,2,3] H/D scrambling reactions of Cp^*_2LnR systems (Ln = Sc, Y, Lu) with alkanes are reported to be slow in contrast to the metallation of alkanes wich is well known for these complexes. For arenes however, both metallation and H/D scrambling is observed which is in agreement with the outcome of our calculations.

Concluding Remarks

In this study we have shown that H/H (H/D) exchange between $(Cp^*_2LnH)_2$ (Ln = Lu, Y) and arenes can be explained in terms of sigma-bond metathesis via transition state **1** involving a direct single step H/H (H/D) exchange (Figure 1). For arenes this process can effectively compete with the conventional sigma-bond metathesis via transition state **2** leading to metallation of arene. For alkanes the situation is different. Here metallation is more favorable and direct H/H (H/D) exchange is not expected to compete indicating that the direct H/H (H/D) exchange reaction depends strongly on the hydrocarbon molecule. These results are in close agreement with experimental observations.

Computational Details

Extended Hückel calculations were carried out using the weighted H_{ij} formula.[9] The atomic parameters used for Lu[10], C and H[11] are those shown in Table I and were taken from the literature. The Lu 4f orbitals were left out of the calculations since it has been shown that they are chemically insignificant.[5,10] For Y, no reported parameters were available. Therefore an estimate was made using the values of Zr[12] with H_{ii} = -10.5 eV for the d levels. The bonding distances and angles used were as follows: Lu-C(Cp) = 2.85 Å, C(Cp)-C(Cp) = 1.42 Å, C-H = 1.09 Å, Lu-H = 1.90 Å, Lu-C(Ph) = 2.60 Å, C(Ph)-C(Ph) = 1.40 Å, Lu-C(Me) = 2.60 Å, Cp-Lu-Cp = 130°, H(Me)-C(Me)-H(Me) = 109.47°, H(Ph)-C(Ph)-H(Ph) = 120°, C(Ph)-C(Ph)-C(Ph) = 120°.

Table I. Parameters Used in Extended Hückel Calculations.

Orbital		H_{ii} (eV)	ζ_1	ζ_2[a]	c_1	c_2
Lu	6s	-6.05	1.666			
	6p	-6.05	1.666			
	5d	-5.12	2.813	1.210	0.7044	0.4880
Y[b]	5s	-9.87	1.817			
	5p	-6.76	1.776			
	4d	-10.50	3.835	1.505	0.6210	0.5769
C	2s	-21.40	1.625			
	2p	-11.40	1.625			
H	1s	-13.60	1.300			

[a] For the d orbitals a double expansion of Slater orbitals was used. [b] An estimate for the Y parameters was made (see text).

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8 The energy level diagram has been described before.[5] These authors have shown that the Lu 4f orbitals can be omitted from the calculations because they are low lying and essentially nonbonding. We used the same simplification in our study.

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Chapter 4

Insertion Chemistry of Cp^*_2Y(2-pyridyl) and Molecular Structure of an Unexpected CO Insertion Product $(Cp^*_2Y)_2(\mu\text{-}\eta^2;\eta^2\text{-}OC(NC_5H_4)_2)$

Introduction

The activation of C-H bonds and the subsequent functionalization of hydrocarbons is a field of considerable current interest in organometallic chemistry. Oxidative addition of C-H bonds with late transition metals is well known[1] and more recently, the heterolytic activation of these bonds by electrophilic high-valent early transition metal complexes has been developed.[2] Especially interesting in this area are the very electrophilic group 3 compounds (including the lanthanides).

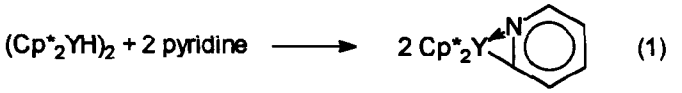
Recently we have shown that group 3 and lanthanide alkyl and hydride complexes very easily activate aromatic C-H bonds in a wide variety of substrates leading to metallacycles containing new M-C bonds.[3] Insertion of unsaturated substrates in metallacyclic M-C bonds is very interesting since it might lead to C-C coupling at the aromatic ring. Especially when the metallation step can be performed in a regio-selective fashion, such a process could be of interest for organic synthesis and provide an alternative for the well-known Pd-mediated functionalization of C-H bonds like the Heck type reaction.[4]

Jordan *et al.* nicely demonstrated a zirconium mediated functionalization of pyridines based on cationic Cp_2Zr(2-pyridyl)$(L)^+$ systems.[5] Recently we found that the hydride $(Cp^*_2YH)_2$ gives facile cyclometallation with a variety of arenes including pyridine,[6] which offers opportunities for the functionalization of arenes and heterocycles. This led us to study the reactivity of the cyclometallated products towards a variety of (unsaturated) substrates. In this chapter we focus on the insertion chemistry of the pyridyl complex Cp^*_2Y(2-pyridyl) (1) and compare it with the isoelectronic Cp_2Zr(2-pyridyl)$(L)^+$.[5]

This work has been performed in collaboration with W.M. Stevels. The X-ray structure determination was performed by M.T. Lakin and A.L. Spek from the University of Utrecht.

Results and Discussion

Synthesis and Properties of Cp^*_2Y(2-pyridyl) (1). When $(Cp^*_2YH)_2$ was allowed to react with pyridine, compound 1 could be isolated in 55 % yield (eq 1).[7] The ^1H- and ^{13}C-NMR spectra of 1 show resonances for the *ortho* C-H fragment (8.02 and 145.27 ppm, respectively) upfield from those of free pyridine (8.53 and 150.0 ppm, respectively). Since the NMR spectra of 1 are in close analogy with those of the corresponding Sc and Lu complexes,[8] in which the pyridyl ligand was found to be η^2-bonded to the metal center by X-ray diffraction, we assume an analogous bonding for the pyridyl ligand in our yttrium compound.

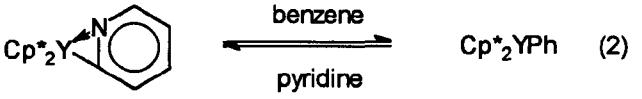


(1)

1

Compound 1 dissolves well in organic solvents like pentane, cyclohexane, benzene and toluene and 1 is thermally very robust. No thermal decomposition was observed after 24 h at 120 °C in benzene-d_6. However, extensive H/D scrambling between the pyridyl ligand and solvent had taken place and no resonances of the pyridyl ligand were observed in the ^1H-NMR spectrum. The Cp* ligands were unaffected. This H/D scrambling is only operative at relatively high temperatures; at 75 °C (24 h) no H/D scrambling was detected.

H/D scrambling most likely involves metallation of solvent producing Cp^*_2YPh and free pyridine in an equilibrium reaction (eq 2). Such an equilibrium should strongly favor the starting compound since in the ^1H-NMR spectrum no indication for the presence of Cp^*_2YPh was observed. The observation that H/D scrambling is not restricted to the *ortho* positions but that other positions are affected as well, suggests that also *meta* and *para* metallated yttrium pyridyl species are involved and are kinetically within reach.

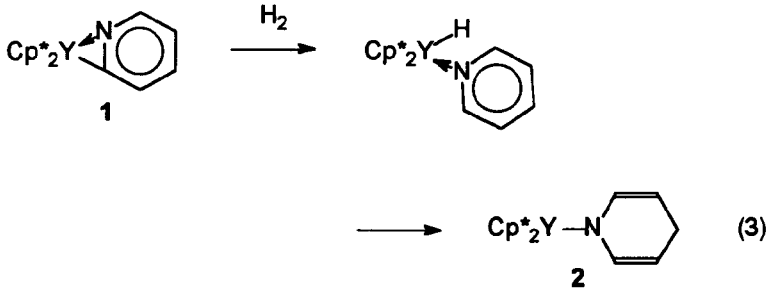


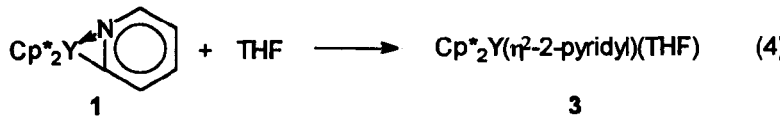
(2)

1

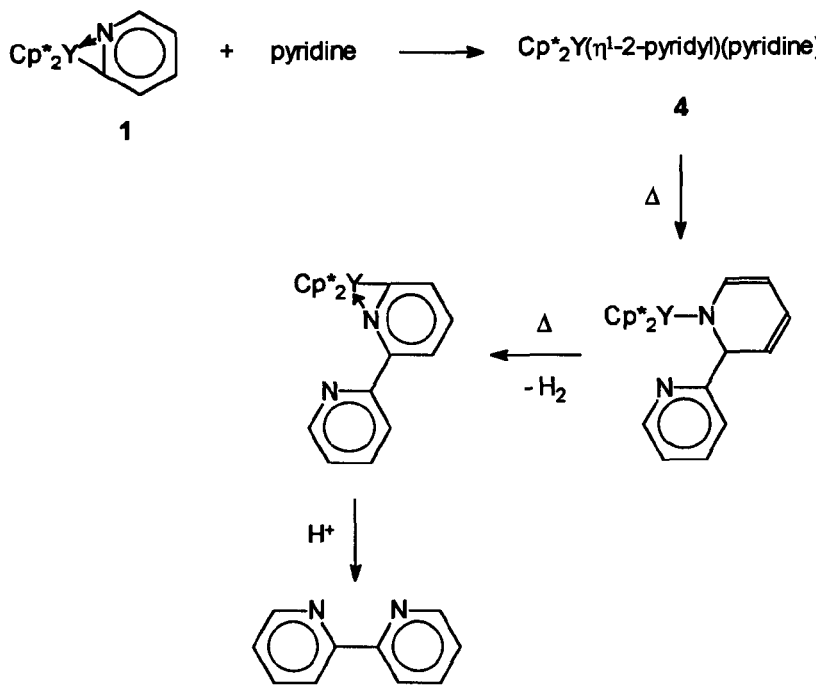
Reaction with Hydrogen. With H_2 (1 bar), **1** reacts in about 3 d at room temperature to form in 50 % yield the 1,4-hydride addition product $Cp^*_2Y(NC_5H_6)$ (**2**) and some unidentified material (eq 3). A comparable observation has been made in the reaction of $[Cp_2YH(THF)]_2$ with pyridine in THF.[9] Here the first step is the formation of the 1,2-addition product which is slowly converted into the 1,4-isomer. Therefore we propose that the first step in eq 3 is hydrogenolysis of the Y-C bond of **1** to form an intermediate hydride pyridine adduct, which then reacts further to the 1,4-addition product **2**. In the Ziegler alkylation of pyridines by alkyllithium,[10] intermediate 1,2-addition products have been observed. In our case, however, no indication for a 1,2-addition product was found, suggesting that the reaction involves direct 1,4-addition. Nucleophilic attack on both the 2 and the 4-position is well-known for pyridine rings.[10b] The unidentified material in the reaction mixture was due to reaction of **1** with pyridine. The ^{1}H-NMR signals of this unidentified compound were identical to those observed in the reaction of **1** with pyridine in the absence of H_2 (*vide infra*).

Reaction with Lewis bases. The Lewis acidity of **1** was tested by studying the complexation behavior towards Et_2O, THF and pyridine. No complexation of Et_2O was observed but with the stronger bases, THF and pyridine, the 1:1 adducts $Cp^*_2Y(\eta^2$-2-pyridyl)(THF) (**3**) and $Cp^*_2Y(\eta^1$-2-pyridyl)(NC_5H_5) (**4**) were formed (eq 4 and Scheme I). The strong downfield shift of the H6 resonance of **4** relative to the corresponding resonance of **1** (8.50 ppm for **4** vs 8.02 ppm for **1**) is close to that of the *ortho* protons of free pyridine (8.53 ppm) and suggests that the pyridyl ligand is η^1-bonded to Y. With Et_2O and THF no further reaction was observed, even when heated at 80 °C for several days.





Scheme I

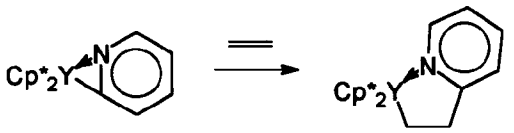


The pyridine adduct, on the other hand, is not very stable and converts in the course of 3 d at 50 °C into a mixture of products. In the ^{1}H-NMR spectrum of this mixture several olefinic signals were present in the region between 6 and 3 ppm indicating that the reaction involves partial reduction of a pyridine ring. Isolation and purification of these products on a preparative scale was severely hampered by the high solubility in hydrocarbon solvents, however. When performed with an excess of pyridine (10 equivalent), analysis of the reaction mixture by GC/MS and ^{1}H-NMR after quenching with water revealed the formation of a stoichiometric amount of 2,2'-bipyridine (1 equivalent per Y), indicating that C-C coupling

between the pyridyl ligand and pyridine had taken place. The amount of 2,2'-bipyridine did not increase after prolonged heating, which means that the reaction is not catalytic under these conditions.

This formation of 2,2'-bipyridine is remarkable since to our knowledge no examples of dehydrogenative C-C coupling reactions with arenes are known for group 3 and 4 organometallic compounds. There is a precedent in organolithium chemistry, where attempted lithiation of pyridine with lithium diisopropylamide also led to the formation of 2,2'-bipyridine.[11] Another example is the alkylation or arylation of pyridine mentioned above, which involves the 1,2-addition of RLi and subsequent elimination of LiH. Therefore Scheme I gives a plausible reaction sequence which also explains the reduction of pyridine. The close analogy with eq 3 also supports the proposed addition step.

Reaction with Alkenes. With excess ethylene, **1** reacts to form the mono-insertion product $Cp^*_2YCH_2CH_2(2\text{-}NC_5H_4)$ (**5**) (eq 5). The conversion is complete within 1 h at room temperature and no further insertion of ethylene is observed (*vide infra*). Reaction with propylene is slower (4 d at 60 °C) and leads selectively to the 1,2-insertion product $Cp^*_2YCH_2CHMe(2\text{-}NC_5H_4)$ (**6**) (eq 6). For both **5** and **6** the nitrogen lone pair of the pyridyl group is expected to coordinate to the metal since the chemical shift of the hydrogen atoms in the *ortho* position to N are different from that of free pyridine and 2-ethylpyridine (δ = 7.45 ppm for **5** and **6** vs 8.53 ppm for free pyridine). The close spectroscopic analogy with $Cp_2ZrCH_2CH_2(2\text{-}NC_5H_3(6\text{-}Me))^+$ where intramolecular coordination of the pyridine function has been found,[5a] supports this.



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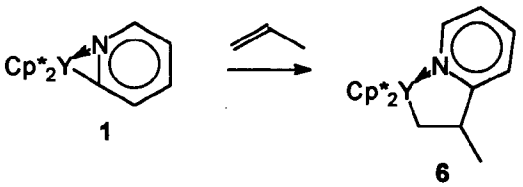


1 6 (6)

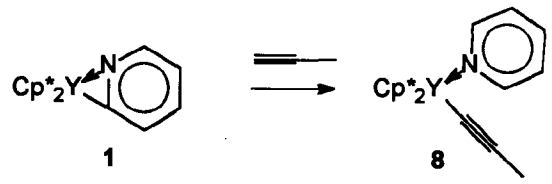
The stability of the 5-membered ring towards consecutive insertion of olefin is remarkable bearing in mind the high activity of M-H and M-C (M = group 3 element) bonds towards the polymerization of olefins.[12] The higher stability of 5-membered rings compared to compounds with larger or smaller ring size is very well known in cyclometallation reactions.[13] Apparently the metallacycles **5** and **6** are stabilized towards further reaction with olefin.[14]

No reaction of **1** with butadiene (1 bar) was observed (3 d at 75 °C).

Reaction with Alkynes. Acetylene reacts with **1** by C-H activation and formation of pyridine (eq 7). The organoyttrium species was identified as the monomeric pyridine acetylide complex $Cp^*_2Y(CCH)(py)$ **7** and was obtained in 29 % yield. The formation of monomeric **7** is unique since the only yttrium ethynyl complex known so far, $\{[C_6H_5C(NSiMe_3)_2]_2Y(\mu\text{-}CCH)\}_2$,[15] is a dimer whereas the scandium analogue, Cp^*_2ScCCH,[16] has only been observed by NMR. Clearly the coordinated pyridine stabilizes **7** as a monomer. It also inhibits catalytic activity since in contrast to Cp^*_2ScCCH, polymerization of the excess of acetylene to polyacetylene has not been observed.

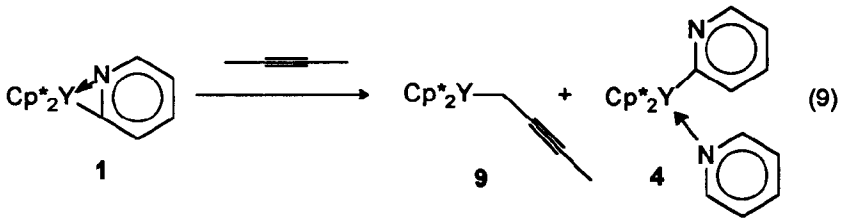
(7)

Also with excess of propyne (1 bar), C-H activation took place to form acetylide $Cp^*_2Y(CCMe)(py)$ **8** (68 % yield) which is again monomeric due to coordination of pyridine (eq 8). In contrast to what was observed for $Cp^*_2YCH(SiMe_3)_2$,[6] no dimerization of propyne is found here, again indicating that the coordinated pyridine effectively blocks catalytic activity.



(8)

To investigate the reactivity of **1** towards internal C-C triple bonds, **1** was allowed to react with 2-butyne and 2-pentyne. With 2-butyne the major reaction was propargylic metallation to form $Cp^*_2YCH_2CCMe$ (**9**)[17] and pyridine (eq 9). The pyridine formed is coordinated to **1** which results in only 50 % conversion of the starting material. As stated before the pyridine adduct **4** is not very stable and starts to decompose under the reaction conditions applied. Adduct **4** is apparently resistant towards decomplexation of pyridine because with an excess of 2-butyne (20 equivalent) still only 50 % conversion was reached. Another remarkable observation is that the pyridine gets coordinated to **1** and not to the metallation product as in eq 8.

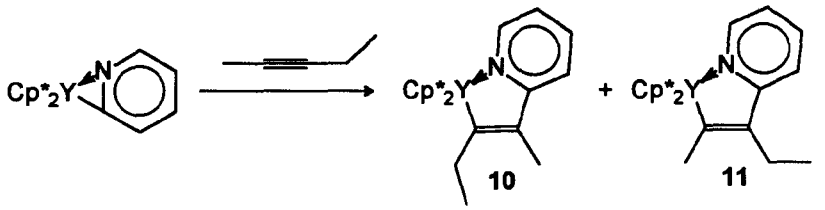


(9)

When the reaction of **1** with 2-pentyne was monitored by ^{1}H-NMR spectroscopy it was found that within 2 d at 75 °C **1** had been converted completely into a mixture of products.[18] The identity of this mixture could not be determined, but the appearance of a quartet at δ = 2.42 ($^3J_{HH}$ = 7.3 Hz) and two triplets at δ = 1.13 and δ = 1.09 ($^1J_{HH}$ = 7.3 Hz for both signals), indicates the presence of a $CH_3CH_2C{=}C$ moiety and suggests that 2,3- and 3,2-insertion of 2-pentyne has taken place (70 %). Attempts to purify the insertion products by crystallization were unsuccessful. Therefore the product mixture was quenched with water and the pyridyl containing organics were purified by acid/base extraction. Analysis of the resulting oil by GC, GC-MS and ^{1}H-NMR showed it to consist of 2,2'-bipyridine, 2-(1-methyl-1-butenyl)pyridine and 2-(1-ethyl-1-propenyl)pyridine (molar ratio: 1.0 : 1.5 : 1.9).

From the presence of 2-(1-methyl-1-butenyl)pyridine and 2-(1-ethyl-1-propenyl)pyridine in the reaction mixture after quenching we conclude that the major reaction is insertion of 2-pentyne to form the regio isomers $Cp^*_2YCEtCMe(2\text{-}NC_5H_4)$ (**10**) and $Cp^*_2YCMeCEt(2\text{-}NC_5H_4)$ (**11**) in a 1.0 : 1.3 ratio (63 %, eq 10). The fact that **11** is the major isomer can be understood on the basis of steric factors favoring the isomer with the larger alkyl substituent on the β-

carbon.[6] The formation of 2,2'-bipyridine is most likely the result of propargylic C-H activation of 2-pentyne analogous to eq 9. The pyridine liberated during this process could then enter the C-C coupling reaction with 1 (Scheme I). Based on the amount of 2,2'-bipyridine formed, propargylic C-H activation accounts for 37 % of the reaction of 1 with 2-pentyne and is far less important than in the case of 2-butyne.



(10)

Electronically, the triple bonds in 2-butyne and 2-pentyne are not very different and therefore this is not expected to cause a drastic change in selectivity. It seems that steric hindrance in the transition state for C-H activation of 2-pentyne is more severe. For C-H activation of 2-pentyne in the 1-position, the ethyl group has to be situated between the wedge of the Cp* ligands, which will be sterically unfavorable. For 3,2-insertion the 2-pentyne molecule can be situated more out of the wedge of the Cp* ligands leading to less steric hindrance and in the case of 2,3-insertion no interaction of the ethyl group with the Cp* ligands is expected. These effects could lead to a reversal of the selectivity going from 2-butyne to 2-pentyne. Another explanation could be the unique allene structure of **9**[17] which apparently also inhibits coordination of pyridine. When this structure is less preferred for metallated 2-pentyne as a result of the larger alkyl substituent, insertion of alkyne might be able to compete.

From these results it can be concluded that the intramolecular coordination of the pyridyl group of **1** has little effect on the reactivity of the Y-C bond towards alkynes because similar C-H activations were observed for $Cp^*_2YCH(SiMe_3)_2$ and $(Cp^*_2YH)_2$.[6,17,19] Compared to $Cp^*_2YCH(SiMe_3)_2$, which shows no reaction with 2-butyne and other disubstituted alkynes, **1** is more reactive however. In addition, the stabilization of the monomeric metallation products by the pyridine formed is quite different from the reactions with Cp^*_2YR and $(Cp^*_2YH)_2$, which led to dimeric acetylides.

Reaction with Carbon Monoxide. Group 3 alkyl complexes normally react with CO to form unstable η^2-acyl compounds which, in the presence of excess CO, enter a consecutive reaction with a second equivalent of CO to form dinuclear enedione diolate complexes.[20] Ketene intermediates are believed to be involved in this second step but conclusive evidence has not yet been obtained. In view of the ability of the pyridyl ligand in **1** to stabilize insertion products we reasoned that it might be possible to capture an intermediate in the reaction of **1** with CO. We were able to isolate a product formed by consecutive reaction of the η^2-acyl but this was not the expected ketene or acyl intermediate.

Both with excess (1 bar) and 1 equivalent of CO **1** reacts in 24 h to form an intensely purple compound $(Cp^*_2Y)_2(\mu\text{-}\eta^2;\eta^2\text{-}OC(2\text{-}NC_5H_4)_2)$ **(12)**. The ^1H- and ^{13}C-NMR spectra of this compound show a 2-substituted pyridine ligand and two inequivalent Cp* rings. A strong IR absorption at 1406 cm^{-1} indicates a severely reduced bond order of the carbonyl functionality.[21] Since these data were not sufficient to identify the structure of **12**, a crystal structure determination was undertaken.

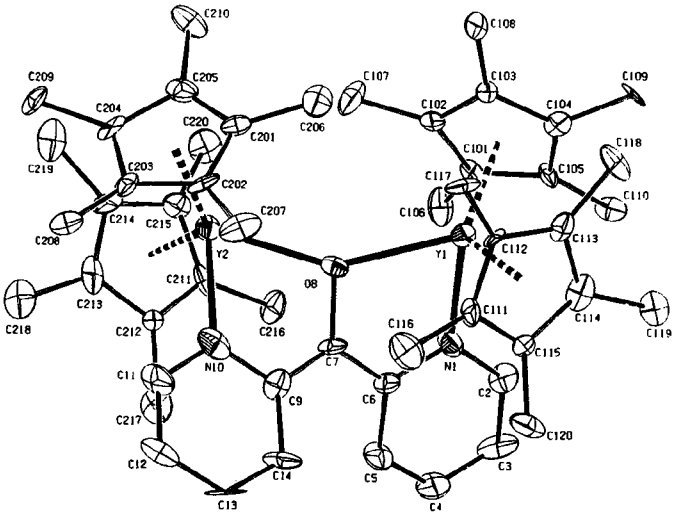


Figure 1. *ORTEP* view drawn at the 50 % probability level and atom-labeling scheme for $(Cp^*_2Y)_2(\mu\text{-}\eta^2;\eta^2\text{-}OC(2\text{-}NC_5H_4)_2)$ **(12)**.

Table I. Selected Bond Distances (Å) and Angles (°) for $(Cp^*_2Y)_2(\mu\text{-}\eta^2;\eta^2\text{-}OC(2\text{-}NC_5H_4)_2)$ (12).[a]

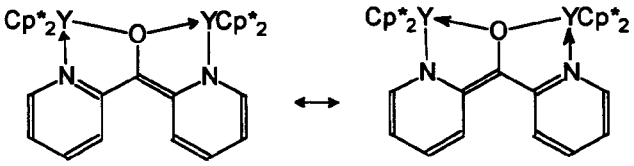
Y1-O8	2.356(8)	C5-C6	1.437(16)
Y1-N1	2.348(9)	C6-C7	1.422(18)
Y2-O8	2.353(8)	C7-C9	1.410(18)
Y2-N10	2.344(9)	C9-C14	1.427(16)
O8-C7	1.424(13)	C11-C12	1.373(17)
N1-C2	1.372(17)	C12-C13	1.41(2)
N1-C6	1.381(16)	C13-C14	1.33(2)
N10-C9	1.386(17)	Y1-Ct1	2.428(5)
N10-C11	1.344(18)	Y1-Ct2	2.416(6)
C2-C3	1.333(17)	Y2-Ct3	2.414(5)
C3-C4	1.39(2)	Y2-Ct4	2.409(5)
C4-C5	1.341(18)		
O8-Y1-N1	72.0(3)	C2-N1-C6	118(1)
O8-Y2-N10	71.7(3)	Y2-N10-C9	111.4(8)
Y1-O8-Y2	149.4(3)	Y2-N10-C11	127.3(9)
Y1-O8-C7	105.4(7)	C9-N10-C11	119(1)
Y2-O8-C7	105.1(7)	Ct1-Y1-Ct2	131.5
Y1-N1-C2	128.7(8)	Ct3-Y2-Ct4	135.4
Y1-N1-C6	111.2(7)		
C6-C7-O8-Y1	-39(1)	C9-C7-O8-Y1	140.1(9)
C6-C7-O8-Y2	139.3(9)	C9-C7-O8-Y2	-42(1)

[a] Ct1 = C101-C105 centroid, Ct2 = C111-C115 centroid, Ct3 = C201-C205 centroid, Ct4 = C211-C215 centroid.

The molecular structure consists of two normal bent Cp^*_2Y units that are bridged by a $\mu\text{-}\eta^2;\eta^2$-dipyridylketone fragment (Figure 1) and is close to C_2 symmetry which explains the two Cp* resonances in the NMR spectra. The Y1-O8 and Y2-O8 distances (Table I) are in the range for bridging alkoxide ligands while the C7-O8 distance is close to that of a C-O single bond (1.43 Å). The C6-C7 and C7-C9 distances clearly posess some double bond character[22] while the Y1-N1 and Y2-N10 bond lengths are close to that of a Y-N sigma bond. The Y-N distances compare

well with those in $[(C_5H_4R)_2Y(HCNCCMe_3)]_2$ (2.325(4) Å) in which Y-N single bond character has been established,[23] and with the Y-N bond distances in $[(C_5H_4R)_2Y(N{=}CHR)]_2$ (2.314(9) and 2.386(1) Å).[9] However, the Y-N single bonds distances in $Cp^*_2YN(SiMe_3)_2$ (2.274(5) and 2.253(5) Å)[24] are significantly shorter.

In addition, both the geometries around O8 and C7 are sp^2, although there is a torsion angle of 39(1)° along C6-C7-O8-Y1. Also the planes of the two pyridyl rings are twisted by 36(6)° relative to each other which is most likely the result of minimizing the strain energy in the two 5-membered metallacycles. As a result these metallacyclic rings are slightly puckered. Based on these data we would describe the structure as intermediate between the two resonance forms depicted in Figure 2. This description explains the short Y-N interactions and the partial double bond character of C6-C7 and C7-C9 caused by the delocalized π system. Also the low ν_{CO} is in agreement with this structure in which the dipyridylketone fragment has formally undergone two electron reduction relative to the free ketone.

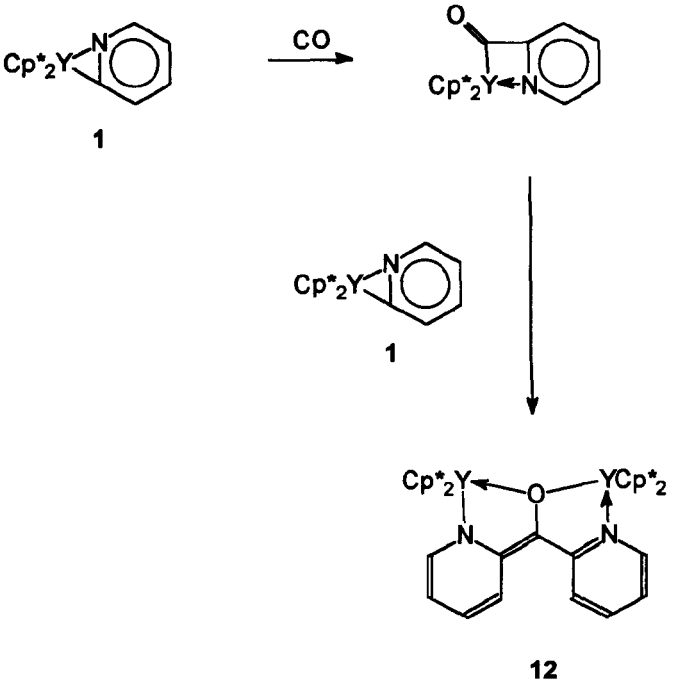


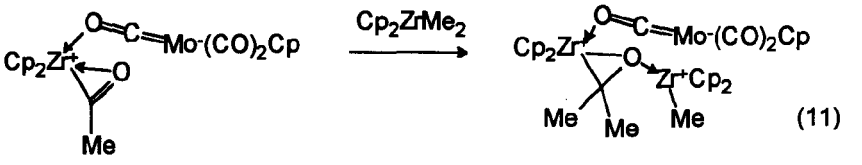
12

Figure 2. Two resonance forms of $(Cp^*_2Y)_2(\mu\text{-}\eta^2;\eta^2\text{-}OC(2\text{-}NC_5H_4)_2)$ **(12).**

The formation of compound **12** is remarkable because the common reaction path seen for group 3 alkyl complexes is insertion of a second equivalent of CO to form ene dione diolate complexes. However for **1**, even with excess of CO, only product **12** is observed (^{1}H-NMR). The product formation can be explained by a scheme in which nucleophilic attack of the starting compound on the acyl species takes place (Scheme II). Such a nucleophilic attack on M(η^2-acyl) and formation of ketone complexes has some precedent in a hetero bimetallic Zr-Mo acyl complex in which a Zr-Me bond has added across the CO bond of the acyl functionality[25] (eq 11). The nucleophilic attack on the acyl has been associated with the presence of a good sigma donating ligand in this system.

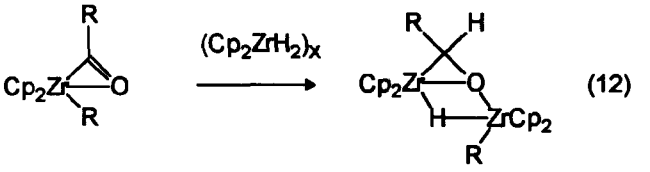
Scheme II





(11)

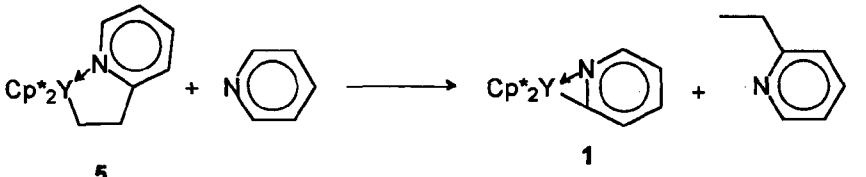
Also the formation of aldehyde complexes from nucleophilic attack on the acyl carbon has been observed (eq 12).[25] In all cases one of the metal centers forms a sigma bond with the former acyl carbon atom. For **12** there is no interaction of C7 with either of the yttrium centers. This can be explained by the delocalized π-system of the pyridyl rings and C7 which leads to increased sigma bond character in the Y-N bonds.



(12)

Nucleophilic attack on acyl carbon atoms has been explained in molecular orbital terms by Hoffmann *et al.*[27] These authors showed that acyl carbon atoms of early transition metal η^2-acyls are electrophilic rather than carbenic in character due to a low lying π^*_{CO} orbital and therefore might show carbenium-type reactivity. The fact that **12** shows no tendency to react with another equivalent of CO is evidently again caused by the donor properties of the pyridyl ring which results in the formation of (two) stable 5-membered metallacycles similar to the insertion reactions with ethylene and propylene. The interaction of **1** with CO is another example in which the Y-pyridyl bond reacts in a totally different manner compared to unfunctionalized Ln-C bonds.

Reactivity of $Cp^*_2YCH_2CH_2(2\text{-}NC_5H_4)$ (5) and Catalytic Conversion of Pyridine to 2-Ethylpyridine. When the starting compound **1** can be regenerated from **5** by hydrogenolysis of the Y-C bond and subsequent metallation of pyridine, catalytic formation of 2-ethylpyridine from pyridine might become feasible. This strategy has been successfully exploited by Jordan *et al.* for $Cp_2Zr(2\text{-pyridyl})(L)^+$ systems.[28] An even simpler method for the regeneration of **1** from **5** would be direct sigma-bond metathesis of **5** with pyridine (eq 13). As anticipated, this regeneration of **1** with pyridine (3 equivalent) was possible (50 °C, 2 d). However, the slower consecutive reaction of **1** with excess pyridine took place as well (*vide supra*).



5 **1**

(13)

With the necessary steps available, catalytic conversion of pyridine to 2-ethylpyridine was attempted. In an experiment under catalytic conditions (40 bar

ethylene, [1]:[pyridine] = 1:33, 110°C) it was found that the pyridine was converted into 2-ethylpyridine (44 %) and small amounts of 2-*n*-butylpyridine (4 %) and 2-*n*-hexylpyridine (traces) were present (GC/MS, ^{1}H-NMR). Also a small amount of polyethylene (IR) was formed indicating that multiple insertions are possible. The remainder of the pyridine was left unreacted.

A probable catalytic cycle is depicted in Fig. 3 which consists of the two reaction steps observed under non-catalytic conditions. The formation of small amounts of 2-*n*-butylpyridine, 2-*n*-hexylpyridine and polyethylene can be explained by multiple insertions of ethylene into the Y-C bond of **5**. Since **5** was found to be very stable towards insertion of ethylene, polymerization with a very low rate of initiation is expected to be operative.[29] When one ethylene molecule has been inserted, polymerization is triggered because now the stabilizing coordination of the pyridyl ring is lifted. After initiation, chain termination by sigma-bond metathesis with pyridine is apparently insignificant since, except for 2-*n*-butylpyridine and 2-*n*-hexylpyridine, no other low molecular weight oligomers were found. In the products from the initiation and the first propagation step there is apparently still some stabilization through coordination of the pyridyl ligand present, which allows chain termination by sigma-bond metathesis with pyridine to compete, resulting in the formation of 2-*n*-butylpyridine and 2-*n*-hexylpyridine.

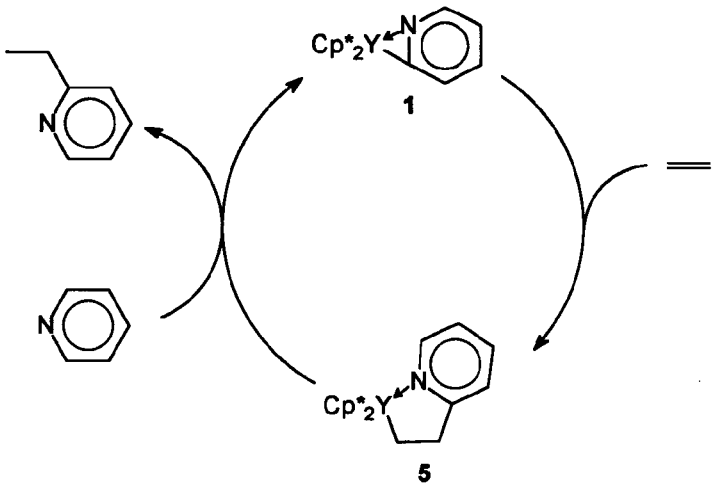
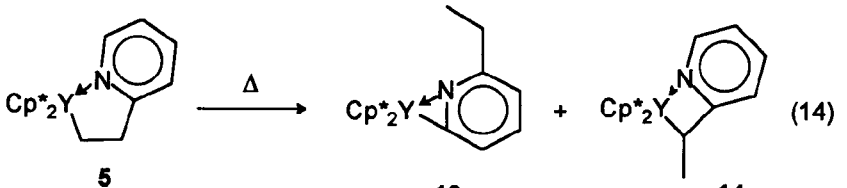


Figure 3. Catalytic cycle for formation of 2-ethylpyridine from pyridine and ethylene.

Finding the optimal reaction conditions for this catalytic alkylation of pyridine is the subject of our current research along with the functionalization of other arenes and heterocycles. It is clear that, in contrast to $Cp_2Zr(2\text{-pyridyl})(L)^+$ systems,[5] in our yttrium system hydrogen is not necessary for regeneration of the catalyst.

To investigate which organo-yttrium species are present under the catalytic reaction conditions, the thermal stability of **5** was examined. It was found that **5** reacts in 4 d at 80 °C to a mixture of the two isomers $Cp^*_2Y(2\text{-}NC_5H_3(6\text{-Et}))$ (**13**) and $Cp^*_2YCHMe(2\text{-}NC_5H_4)$ (**14**) (ratio 60 : 40, eq 14). No attempts were made to isolate these compounds because of they could be completely identified on the basis of NMR data. The rate of thermolysis was enhanced when Lewis bases THF or Et_2O were added in stoichiometric amounts (see experimental section). During the reaction, no Lewis base adducts of **5** were observed in the ^{1}H-NMR spectrum, however.

The formation of **13** and **14** may involve the generation of an incipient fulvene species $Cp^*(\eta^6\text{-}CH_2C_5Me_4)Y$ which metallates 2-ethylpyridine in both the benzylic and the *ortho* positions. Evidence of intermediate $Cp^*(\eta^6\text{-}CH_2C_5Me_4)Y$ has been obtained in the thermolysis of $Cp^*_2YCH(SiMe_3)_2$[6,30] and in benzene and methane metallation reactions of $(Cp^*_2YMe)_2$[31] under similar reaction conditions. The rate enhancement with added Lewis base suggests that decomplexation of the pyridyl group might be necessary for Cp* activation to take place. The Lewis base might stabilize an intermediate $Cp^*_2YCH_2CH_2(2\text{-}NC_5H_4)$ species in which the intramolecular coordination of the pyridyl group has been lifted. This would allow the Y-CH_2 fragment to reach the favored orientation for Cp* ligand metallation. Isomerization of **5** to **13** and **14** is also expected to take place in the catalytic formation of 2-ethylpyridine, which might lead to deactivation of the catalyst.



(14)

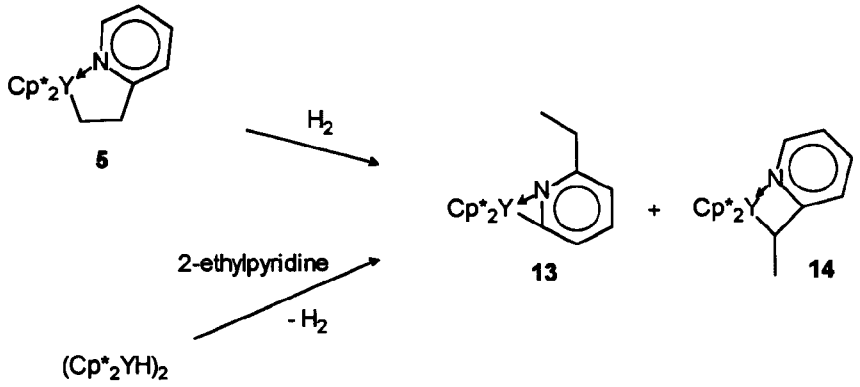
5 **13** **14**

60 : 40

Regeneration of **1** from **5** with H_2 was also tried, but this again resulted in the formation of a mixture of **13** and **14** with a slightly different product ratio however

(45 :55, Scheme III). Since this reaction is expected to involve the formation of a Y-H bond by hydrogenolysis, we also reacted the hydride $(Cp^*_2YH)_2$ with 2-ethylpyridine and a similar product distribution was found (Scheme III). This confirms the formation of a common hydride intermediate for both reactions. From this it is clear that hydrogenolysis of the Y-C bond in **5** is not a good route for the regeneration of **1** since it leads to the formation of other metallation products.

Scheme III



Concluding Remarks

The Y-pyridyl bond in **1** is in principle very reactive but this reactivity seems to be limited to small molecules because of steric saturation at the yttrium center. Insertions of olefins and alkynes are especially sensitive to this steric inaccessibility of the yttrium center which prevents approach of the π-system of these substrates; a prerequisite for insertion. However, when using small molecules like CO, ethylene and propene, interesting reactivity of the insertion products is observed leading to unexpected compounds. The use of a sterically less demanding ligand system or a larger metal center (a lanthanide for instance) might result in a wider scope for this chemistry by allowing the insertion of alkynes in the Y-pyridyl bond.

Experimental Section

General Considerations. All experiments were performed under nitrogen using standard Schlenk, glovebox (Braun MB200), and vacuum line techniques. Pentane, THF, cyclohexane, benzene, benzene-d_6, toluene-d_8, were distilled from Na/K alloy and degassed prior to use. $Cp^*_2YCH(SiMe_3)_2$ and $(Cp^*_2YH)_2$ were prepared according to published procedures.[6] H_2 (99.9995%, Hoek-Loos), ethylene, propylene, acetylene, CO (UCAR), butadiene and propyne (Matheson) were used without further purification. Pyridine and 2-ethylpyridine were distilled from KOH. Other reagents and cyclohexane-d_{12} were stored over mol sieves (4 Å) and degassed prior to use. Chloroform-d_1 was used as purchased.

NMR spectra were recorded on Gemini 200 (^{1}H: 200 MHz) and Varian VXR-300 (^{1}H: 300 MHz, ^{13}C: 75.4 MHz) spectrometers at ambient temperatures. GC/MS analyses (EI) were carried out on a Ribermag R 10-10 C instrument using a CP Sil 5 CB column. IR spectra were recorded as Nujol mulls between KBr disks on a Mattson FT-IR spectrophotometer. Elemental analyses were carried out at the Micro-Analytical Department of the University of Groningen. The determinations are the average of two independent determinations.

Synthesis of Cp^*_2Y(2-pyridyl) (1). 5.20 g (10.0 mmol) $Cp^*_2YCH(SiMe_3)_2$ was dissolved in 100 mL of pentane and stirred for 4 h under H_2 (1 bar) at 0 °C. The pentane layer was decanted and the white residu was dried in vacuum. This material was suspended in 30 mL of fresh pentane and 0.80 mL (9.9 mmol) of pyridine was added with stirring. The color of the reaction mixture changed to yellow and gas evolution was observed. After 18 h, volatiles were removed in vacuum and the yellow solid was washed with 2.5 mL of pentane, dissolved in 25 mL of pentane and filtered. Crystallization at - 80 °C yielded 1.86 g (4.25 mmol) yellow crystals. Concentration of the mother liquor yielded a second crop of 0.54 g (1.2 mmol). Total yield 55 %. ^{1}H-NMR (200 MHz, benzene-d_6): 8.02 (d, $^3J_{HH}$ = 5.2 Hz, 1H, pyridyl H), 7.82 (d, $^3J_{HH}$ = 7.2 Hz, 1H, pyridyl H), 7.08 (t, $^3J_{HH}$ = 7.2 Hz, 1H, pyridyl H), 6.64 (m, 1H, pyridyl H), 1.83 (s, 30H, C_5Me_5). ^{1}H-NMR (200 MHz, cyclohexane-d_{12}): δ 8.20 (d, $^3J_{HH}$ = 5.1 Hz, 1H, pyridyl H), 7.70 (d, $^3J_{HH}$ = 7.3 Hz, 1H, pyridyl-H), 7.21 (t, $^3J_{HH}$ = 6.0 Hz, 1H, pyridyl H), 6.86 (t, $^3J_{HH}$ = 6.5 Hz, 1H, pyridyl H), 1.71 (s, 30H, C_5Me_5). ^{13}C-NMR (75.4 MHz, cyclohexane-d_{12}): δ 225.53 (d, $^1J_{CY}$ = 33.2, Y-C), 145.27 (d, $^1J_{CH}$ = 173.9 Hz, pyridyl C), 133.55 (d, $^1J_{CH}$ = 162.0 Hz, pyridyl CH), 133.24 (d, $^1J_{CH}$ = 158.3 Hz, pyridyl

CH), 121.14 (d, $^1J_{CH}$ = 161.1 Hz, pyridyl CH), 116.66 (s, C_5Me_5), 10.63 (q, $^1J_{CH}$ = 125.5 Hz, C_5Me_5). Anal. Calcd for $C_{25}H_{34}NY$: C, 68.64; H, 7.83; Y, 20.32. Found: C, 68.76; H, 7.90; Y, 20.43.

1 could also be prepared directly from $Cp^*_2YCH(SiMe_3)_2$: 1.5 mL (19 mmol) of pyridine was added to a solution of 9.5 g (18 mmol) of $Cp^*_2YCH(SiMe_3)_2$ in 100 mL of pentane. This mixture was stirred for 6 h under H_2 (1 bar) and the light-brown solid which formed was isolated and identified by ^{1}H-NMR. Yield: 5.83 g (13.3 mmol, 73 %).

Reaction of 1 with H_2. A solution of 15 mg (0.034 mmol) of **1** in 0.5 mL of benzene-d_6 was exposed to 1 bar of H_2. The progress of the reaction was followed with ^{1}H-NMR spectroscopy. After 3 d at room temperature **1** had been completely converted into **2** (50 %) and some unidentified material due to reaction of **1** with pyridine (remaining 50 %). ^{1}H-NMR of **2** (300 MHz, benzeen-d_6): δ 5.70 (d, $^3J_{HH}$ = 7.7 Hz, 2H, NCH=), 4.01 (m, 2H, =C*H*-CH_2), 3.10 (t, $^3J_{HH}$ = 2.9 Hz, 2H, CH_2), 1.80 (s, 30H, C_5Me_5).

$Cp^*_2Y(\eta^2$-2-pyridyl)(THF) (3). To a solution of 44 mg (0.10 mmol) of **1** in 0.5 mL benzene-d_6 was added 8.1 μL (0.10 mmol) of THF which resulted in the instantaneous formation of **3**. No decomposition was observed during several days at 80 °C. ^{1}H-NMR (200 MHz, benzene-d_6): δ 8.15 (d, $^3J_{HH}$ = 5.2 Hz, 1H, H6), 7.79 (d, $^3J_{HH}$ = 8.5 Hz, 1H, H3), 7.14 (m, 1H, H4), 6.69 (m, 1H, H5), 3.67 (m, 4H, α-THF),1.84 (s, 30H, C_5Me_5), 1.43 (m, 4H, β-THF).

Reaction of 1 with Pyridine. To a solution of 25 mg (0.057 mmol) of **1** in 0.5 mL of benzene-d_6 was added 4.6 μL (0.057 mmol) of pyridine which resulted in the instantaneous formation of **4**. ^{1}H-NMR (300 MHz, benzene-d_6): δ 8.74 (m, 2H, pyridine *ortho* H), 8.50 (d, $^3J_{HH}$ = 7.1 Hz, 1H, H6), 7.98 (d, $^3J_{HH}$ = 5.1 Hz, 1H, H3), 7.23 (t, $^3J_{HH}$ = 7.1 Hz, 1H, H4), 6.95 (m, 1H, pyridine *para* H), 6.79 (m, 1H, H5), 6.69 (m, 2H, pyridine *meta* H), 1.77 (s, 30H, C_5Me_5). The thermolysis of **4** was monitored by ^{1}H-NMR for several days at 50 °C. After 2 d, **4** had been converted completely into a mixture of unidentified compounds (see text).

Reaction of 1 with Excess Pyridine. To a solution of 50 mg (0.11 mmol) of **1** in 10 mL of cyclohexane was added 180 μL (2.22 mmol) of pyridine. The reaction mixture was stirred for 1 day under reflux and a sample of the mixture was

analyzed by GC and GC/MS after quenching with water and drying over $MgSO_4$. This showed the presence of 2,2'-bipyridine (1 equivalent per Y), pyridine, and Cp*H. GC/MS of 2,2'-bipyridine (EI, 70 eV): *m/e* 157 (15), 156 (100) {molecular ion}, 155 (46), 130 (10), 129 (20), 128 (27), 104 (7), 103 (8), 102 (9), 101 (7), 79 (22), 78 (70), 77 (13), 76 (15), 75 (12), 74 (7), 64 (6), 63 (7), 52 (17), 51 (40), 50 (15), 28 (6). Further heating of the reaction mixture for 3 d did not show any increase in the amount of 2,2'-bipyridine. The remaining reaction mixture was quenched with water and extracted with ether. The ether layer was dried over $MgSO_4$ and volatiles were removed in vacuum. The remaining yellow oil was unequivocally identified by ^{1}H-NMR as a mixture of 2,2'-bipyridine and Cp*H. ^{1}H-NMR of 2,2-bipyridine (300 MHz, chloroform-d_1): δ 8.83 (broad d, $^3J_{HH}$ = 4.0 Hz, 2H), 8.55 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.97 (td, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.8 Hz, 2H), 7.46 (ddd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.1 Hz, 2H).

Synthesis of $Cp^*_2YCH_2CH_2(2\text{-}NC_5H_4)$ (5). A solution of 0.91 g (2.1 mmol) of **1** in 15 mL of pentane was stirred for 1 h under ethylene (1 bar). A yellow precipitate formed and the liquid was filtered off. Yield: 0.54 g (1.2 mmol, 55 %) of a yellow powder. IR (cm^{-1}): 2955 (vs), 2924 (vs), 2857 (vs), 2723 (w), 1599 (s), 1562 (w), 1527 (w), 1462 (s), 1377 (s), 1321 (w), 1282 (m), 1153 (w), 1017 (w), 995 (w), 754 (m), 741 (w), 721 (m), 659 (m), 638 (m), 532 (m). ^{1}H-NMR (300 MHz, toluene-d_8): δ 7.45 (d, 1H, $^3J_{HH}$ = 5.4 Hz, pyridyl H), 6.95 (m, 1H, pyridyl H), 6.67 (d, 1H, $^3J_{HH}$ = 7.8 Hz, pyridyl H), 6.44 (m, 1H, pyridyl H), 3.36 (t, 2H, $^3J_{HH}$ = 7.4 Hz, YCH_2CH_2), 1.97 (s, 30H, C_5Me_5), 0.36 (td, 2H, $^3J_{HH}$ = 7.6 Hz, $^2J_{HY}$ = 3.1 Hz, YCH_2). ^{13}C-NMR (75.4 MHz, toluene-d_8): δ 172.7 (s, pyridyl C), 146.2 (d, $^1J_{CH}$ = 176 Hz, pyridyl CH), 137.7 (d, $^1J_{CH}$ = 157 Hz, pyridyl CH), 124.4 (overlaps with solvent signal, pyridyl CH), 119.7 (d, $^1J_{CH}$ = 165 Hz, pyridyl CH), 115.7 (s, C_5Me_5), 38.1 (t, $^1J_{CH}$ = 123 Hz, YCH_2CH_2), 27.0 (dt, $^1J_{CH}$ = 113 Hz, $^1J_{CY}$ = 49 Hz, YCH_2), 11.3 (q, $^1J_{CH}$ = 125 Hz, C_5Me_5). Anal. Calcd for $C_{27}H_{38}NY$: C, 69.66; H, 8.32; Y, 19.10. Found: C, 69.81; H, 8.28; Y, 19.19.

Synthesis of $Cp^*_2YCH_2CHMe(2\text{-}NC_5H_4)$ (6). 0.959 g (2.19 mmol) **1** was dissolved in 5 mL of cyclohexane and stirred under propylene (1 bar) at 60 °C for 4 days during which the color of the reaction mixture became brown and crystals of the same color formed. Volatiles were removed in vacuum and the remaining solid was extracted once with pentane. The extract was concentrated and crystallization at

-80 °C yielded 0.485 g (1.01 mmol, 46 %) brown crystals. IR (cm^{-1}): 3050 (w), 2924 (vs), 2955 (vs), 2855 (vs), 2722 (w), 1599 (s), 1567 (w), 1462 (s), 1377 (s), 1294 (w), 1161 (w), 1143 (w), 1051 (w), 1013 (m), 976 (w), 962 (w), 779 (m), 752 (m), 737 (m), 723 (m), 642 (w), 602 (w), 521 (w), 500 (w). ^{1}H-NMR (200 MHz, benzene-d_6): δ 7.32 (m, 1H, pyridyl H), 6.93 (m, 2H, pyridyl H), 6.44 (m, 1H, pyridyl H), 3.23 (m, 1H, CH_2CHMe), 1.91 (s, 30H, C_5Me_5), 1.55 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH_2CHMe), 0.60 (m, 1H, YCH), 0.05 (m, 1H, YCH). ^{13}C-NMR (75.4 MHz, benzene-d_6): δ 175.06 (pyridyl C), 145.38 (pyridyl CH), 137.93 (pyridyl CH), 123.03 (pyridyl CH), 119.56 (pyridyl CH), 115.69 (C_5Me_5), 115.61 (C_5Me_5), 41.53 (CH_2CHMe), 40.69 (d, $^1J_{CY}$ = 49.0 Hz, YCH_2), 27.51 ($CHMe$), 11.50 (C_5Me_5), 11.16 (C_5Me_5). Anal. Calcd for $C_{28}H_{40}NY$: C, 70.13; H, 8.41; Y, 18.54. Found: C, 69.69; H, 8.38; Y, 18.58.

Synthesis of $Cp^*_2Y(CCH)(py)$ (7). A stirred solution of 0.54 g (1.2 mmol) of **1** in 20 mL of pentane was cooled to -80 °C and exposed to an atmosphere of acetylene (0.5 bar, 10 equivalent). Then the reaction mixture was allowed to warm to room temperature which resulted in the formation of a red solution. The mixture was stirred at room temperature for 3 d upon which a yellow solid formed. The reaction mixture was cooled to -30 °C and the pentane layer was decanted. The residu was washed with 5 mL of pentane and recrystallized from 30 mL of pentane at -80 °C. Yield: 0.16 g (0.35 mmol, 29 %) of a yellow material. IR (cm^{-1}): 3264 (m), 3059 (m), 2955 (s), 2924 (s), 2854 (s), 2723 (m), 1601 (s), 1489 (sh), 1460 (s), 1446 (s), 1377 (s), 1217 (m), 1066 (m), 1039 (m), 1020 (m), 1008 (m), 756 (s), 721 (m), 705 (s), 659 (s), 626 (s). ^{1}H-NMR (benzene-d_6, 200 MHz): δ 8.59 (broad s, $lw_{1/2}$ = 193 Hz, 2H, *ortho* H's of pyridine), 6.75 (tt, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, *para* H of pyridine), 6.49 (t, $^3J_{HH}$ = 6.8 Hz, 2H, *meta* H's of pyridine), 2.55 (d, $^2J_{HY}$ = 2.1 Hz, 1H, YCCH), 2.02 (s, 30 H, C_5Me_5). ^{13}C-NMR (benzene-d_6, 75.4 MHz): δ 149.37 (d br, *ortho* C's of pyridine), 138.11 (d, $^1J_{CH}$ = 168 Hz, *para* C of pyridine), 124.02 (d, $^1J_{CH}$ = 168 Hz, *meta* C's of pyridine), 117.07 (s, C_5Me_5), 95.34 (dd, $^1J_{CH}$ = 212 Hz, $^2J_{CY}$ = 13 Hz, YCCH), 11.75 (q, $^1J_{CH}$ = 126 Hz, C_5Me_5), α-C resonance not found. Anal. Calcd for $C_{27}H_{36}NY$: C, 69.97; H, 7.83; Y, 19.18. Found: C, 69.43; H, 7.77; Y, 19.10.

Synthesis of $Cp^*_2Y(CCMe)(py)$ (8). A solution of 0.686 g (1.57 mmol) of **1** in 25 mL of pentane was stirred under propyne (1 bar) for 2.5 h. The propyne was replaced by nitrogen and crystallization at -80 °C afforded 0.510 g (1.07 mmol, 68

%) of **7** as brown-yellow crystals. IR (cm^{-1}): 2957 (vs), 2924 (vs), 2903 (vs), 2723 (w), 2069 (w), 1601 (m), 1462 (vs), 1377 (s), 1305 (w), 1217 (m), 1155 (w), 1069 (w), 1038 (w), 1020 (w), 1006 (m), 949 (m), 754 (s), 723 (m), 706 (s), 626 (m), 588 (w). ^{1}H-NMR (300 MHz, benzene-d_6): δ 8.5 (broad singlet, 2H, pyridyl H), 6.77 (m, 1H, pyridyl H), 6.52 (m, 2H, pyridyl H), 2.07 (s, 3H, C≡CMe), 2.03 (s, 30H, C_5Me_5). ^{13}C-NMR (75.4 MHz, benzene-d_6): δ 149.56 (d, $^1J_{CH}$ = 168.1 Hz, 2 pyridyl CH), 138.10 (d, $^1J_{CH}$ = 168.2 Hz, pyridyl CH), 133.68 (d, $^1J_{CY}$ = 70.3 Hz, Y*C*≡CMe), 124.01 (d, $^1J_{CH}$ = 167.0 Hz, 2 pyridyl CH), 116.82 (s, C_5Me_5), 103.30 (dq, $^2J_{CY}$ = 12.7 Hz, $^2J_{CH}$ = 9.2 Hz, YC≡*C*Me), 11.77 (q, $^1J_{CH}$ = 124.4 Hz, C_5Me_5), 6.17 (q, $^1J_{CH}$ = 129.0 Hz, C≡C*Me*). Anal. Calcd for $C_{28}H_{38}NY$: C, 70.43; H, 8.02; Y, 18.62. Found: C, 70.27; H, 8.05; Y, 18.65.

Reaction of 1 with 2-Butyne. 2-Butyne (5.0 μL, 0.064 mmol) was added to a solution of 25 mg (0.056 mmol) of **1** in 0.5 mL of benzene-d_6. After 5 min at room temperature, characteristic resonances of **9** (29 %) were observed in the ^{1}H-NMR spectrum which were identical to those reported earlier.[17] The ^{1}H-NMR spectrum, after 2 h at room temperature, showed no changes. However, after 15 h at 75 °C, 50 % of **9** and 50 % of the unidentified Cp^*_2Y product resulting from reaction of **1** with pyridine were present. Of the 2-butyne 0.64 equivalent remained. Addition of a 20 fold excess of 2-butyne did not lead to an increase of the amount of **9**.

Reaction of 1 with 2-Pentyne. 2-Pentyne (9.0 μL, 0.094 mmol) was added to a solution of 40.3 mg (0.092 mmol) of **1** in 0.6 mL of cyclohexane-d_{12}. The resulting solution was transferred to an NMR tube which was kept at 75 °C. The progress of the reaction was monitored by ^{1}H-NMR and after 2 d the reaction was complete. The NMR tube was opened and the reaction mixture was quenched with 2 mL of water. The mixture was extracted three times with 1 mL of Et_2O. The ether extracts were washed with water and back extracted three times with 0.5 mL of 5 % HCl (aq). The combined extracts were washed with Et_2O and neutralized with 5 N of KOH (aq) upon which a yellow oil formed. This mixture was extracted three times with 0.5 mL of Et_2O, the extract was dried over $MgSO_4$ and volatiles were removed in vacuum affording a yellow oil. ^{1}H-NMR, GC and GC/MS analysis showed this oil to consist of 2,2'-bipyridine, 2-(1-methyl-1-butenyl)pyridine and 2-(1-ethyl-1-propenyl)pyridine (molar ratio: 1.0 : 1.5 : 1.9). ^{1}H-NMR for 2-(1-methyl-1-butenyl)pyridine and 2-(1-ethyl-1-propenyl)pyridine (200 MHz, chloroform-d_1): δ 8.41 (dt, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.3 Hz, H6), 7.62 (tt, $^3J_{HH}$ =

%) and thermolysis products of **4** (35 %) had been formed. Further heating resulted in complete conversion to 2-ethylpyridine and thermolysis products of **4**.

Catalytic Conversion of Pyridine to 2-Ethylpyridine. A solution of 0.33 g (0.76 mmol) of **1** and 2.0 mL (25 mmol) of pyridine in 85 mL of benzene was placed into an autoclave (with glass insert) and pressurized with ethylene (40 bar). After stirring for 18 h at 110 °C, during which the pressure remained essentially constant, the pressure was released and the reaction mixture was quenched with 2 mL of methanol. A sample of the resulting mixture was filtrated and analyzed by GC and GC/MS. The small amount of white material (30 mg) which had been formed, was washed with methanol, dried at 100 °C and identified by IR (KBr pellet) to be polyethylene.[32] End group determination by IR was not possible due to occlusion of water in the polymer.

Thermolysis of $Cp^*_2YCH_2CH_2(2\text{-}NC_5H_4)$ (5). A solution of **5** (25 mg, 0.054 mmol) in 0.5 mL of cyclohexane-d_{12} was kept at 80 °C. The progress of the thermolysis was monitored by ^{1}H-NMR. After 4 d, **5** had been converted completely into a mixture of **13** (60 %) and **14** (40 %). ^{1}H-NMR for **13** (300 MHz): δ 7.50 (pd, $^3J_{HH}$ = 5.6, 1H, H5), 7.20 (t, 1H, H4), 6.77 (d, $^3J_{HH}$ = 7.3 Hz, 1H, H3), 2.69 (q, 2H, CH_2CH_3), 1.72 (s, 30H, C_5Me_5), 1.29 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH_2CH_3). ^{13}C-NMR for **13** (75.4 MHz): δ 224.71 (d, $^1J_{CY}$ = 33 Hz, C2), 159.48 (s, C6), 135.71 (d, $^1J_{CH}$ = 158 Hz, pyridyl CH), 134.05 (d, $^1J_{CH}$ = 157 Hz, pyridyl CH), 119.00 (d, $^1J_{CH}$ = 162 Hz, pyridyl CH), 116.69 (s, C_5Me_5), 31.61 (t, $^1J_{CH}$ = 125 Hz, CH_2CH_3), 13.30 (q, $^1J_{CH}$ = 127 Hz, CH_2CH_3), 10.85 (q, $^1J_{CH}$ = 125 Hz, C_5Me_5). ^{1}H-NMR for **14** (300 MHz): δ 7.28 (pd, $^3J_{HH}$ = 4.9 Hz, 1H, H6), 7.04(m, 1H, H5), 6.60 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H3), 6.12 (m, 1H, H4), 2.46 (pseudo q, J = 5.6 Hz, 1H, $YCHCH_3$), 1.80 (s, C_5Me_5), 1.44 (d, $^3J_{HH}$ = 5.6 Hz, 3H, $YCHCH_3$). ^{13}C-NMR of **14** (75.4 MHz): δ 167.31 (s, C2), 146.06 (d, $^1J_{CH}$ = 171 Hz, C6), 130.95 (d, $^1J_{CH}$ = 162 Hz C4), 117.33 (s, C_5Me_5), 115.50 (d, $^1J_{CH}$ = 158 Hz, C3 or C5), 109.83 (d, $^1J_{CH}$ = 167 Hz, C3 or C5), 47.54 (dd, $^1J_{CH}$ = 130 Hz, $^2J_{CY}$ = 11 Hz, $YCHCH_3$), 11.71 ($YCHCH_3$, overlaps with C_5Me_5 signal), 10.80 (q, $^1J_{CH}$ = 125 Hz, C_5Me_5).

The influence of equimolar amounts of Lewis base on thermolysis was studied at 50 °C in benzene-d_6. The times necessary for complete thermolysis were as follows: THF, 5 d; Et_2O, 10 d; PMe_3, 1 month. In all cases the 60 : 40 ratio of **13** : **14** was observed.

Treatment of 5 with H_2. An NMR-tube containing a solution of **5** (25 mg, 0.054 mmol) in 0.5 mL of benzene-d_6 was exposed to 1 equivalent of H_2 using a vacuum line. After 10 min at room temperature, ^{1}H-NMR (200 MHz) of the yellow solution showed that **5** had been completely converted into a mixture of **13** (45 %) and **14** (55 %).

Reaction of $(Cp^*_2YH)_2$ with 2-Ethylpyridine. To a suspension of 25 mg (0.035 mmol) of $(Cp^*_2YH)_2$ in 0.5 mL of benzene-d_6 was added 7.9 μL (0.070 mmol) of 2-ethylpyridine. Immediately gas evolution was observed and a yellow solution formed. ^{1}H-NMR (200 MHz) showed the quatitative formation of a mixture of **13** (40 %) and **14** (60 %).

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Chapter 5

Activation of Ethers and Sulfides by Organo-Lanthanide Hydrides. Molecular Structure of $(Cp^*_2Y)_2(\mu\text{-}OCH_2CH_2O)(THF)_2$

Introduction

Organometallic compounds of group 3 and the lanthanides are very active in both the polymerization[1] and hydrogenation[2] of olefins. Also the cyclization of 1,4-, 1,5- and 1,6-dienes is very efficiently catalyzed by scandium and yttrium complexes.[3] However in general these catalytic processes have severe limitations, since they can only be performed with non-functionalized olefins. Only very recently some examples appeared of catalytic conversions of olefins bearing functional groups. For instance the hydrogenation of olefins with ether and thioether functionalities can be achieved.[4] Also the cyclization of some functionalized dienes starting from $Cp^*_2YMe(THF)$ can be performed without severe deactivation of the catalyst.[3b] The living polymerization of MMA (methyl methacrylate) by organolanthanides shows that in some cases even carbonyl groups are tolerated.[5]

Some examples of C-X activation have been reported in the literature. For instance the activation of alkyl halides leading to selective dehalogenation has been studied.[6] Several authors have reported on C-O cleavage, which resulted in the formation of Ln-O bonds.[7] The question remains, however, why some functional groups are tolerated in catalytic cycles and others are not. In order to understand fully the processes involved we started a program directed to the interaction of some well-known catalytically active lanthanide hydride complexes $(Cp^*_2LnH)_2$ (Ln = Y, La and Ce) with molecules R-X (X = OR, SR, NR_2, PR_2, COOR, $CONR_2$, etc.).

In this study we focus on C-O and C-S containing molecules. Selective C-O cleavage by transition metal complexes can have considerable impact on organic synthesis.[8] For instance the zirconium-mediated deprotection of allyl protected hydroxyl functions was recently reported.[9] Also C-S bond activation is especially interesting because of its relevance to hydrodesulfurization (HDS).[10] Recently we

The X-ray structure determination was performed by H. Kooijman and A.L. Spek from the University of Utrecht.

showed that C-H activation can compete effectively with C-X activation in substituted arenes.[11] We now direct our attention to non-aromatic and hetero-aromatic substrates. In particular the possible competition between C=C, C-H and C-X activation is an interesting subject.

Results

Activation of Ethers. In an exploratory study the interactions of the group 3 and lanthanide hydrides $(Cp^*_2LnH)_2$ (Ln = Y (**1a**), La (**1b**) and Ce (**1c**)) with ethers (ROR') were studied by ^{1}H-NMR (0.03-0.08 M, benzene-d_6, room temperature). Later some of the experiments were carried out on a preparative scale. In general clean reactions were observed with formation of alkoxides Cp^*_2LnOR and alkane (eq 1, Table I).

$$(Cp^*_2LnH)_2 + 2\ ROR' \longrightarrow Cp^*_2LnOR + Cp^*_2LnOR' + R'H + RH \quad (1)$$

1a: Ln = Y
1b: Ln = La
1c: Ln = Ce

For yttrium, splitting of Et_2O was quantitative when 1 equivalent of Et_2O per Y was applied. Addition of excess Et_2O resulted in the formation of adduct $Cp^*_2YOEt(Et_2O)$ (**3a**). For lanthanum and cerium the products Cp^*_2LnOEt show an increased tendency to complex Et_2O resulting in the formation of the adducts $Cp^*_2LnOEt(Et_2O)$. Dissociation of Et_2O in these adducts appears to be difficult because the complexed ether is unavailable for reaction with **1b** and **1c**. As a consequence, complete conversion of **1b** and **1c** to the alkoxides requires at least 2 eq of Et_2O per Ln. Within a few minutes after addition of a stoichiometric amount of diethyl ether to **1a** in benzene-d_6, resonances were observed which were assigned to an intermediate ether adduct $Cp^*_2YD(Et_2O)$.[12] This intermediate was completely converted to Cp^*_2YOEt (**2a**) and ethane as the reaction progressed.

In principle ether splitting is a good synthetic method for the preparation of the ether free alkoxide **2a** and ether adducts $Cp^*_2LnOEt(Et_2O)$ (Ln = La (**3b**) and Ce (**3c**)). However, with increased steric bulk of the ether substituents the rate of cleavage decreased dramatically. The half-lifetimes of **1a** with different ethers were determined as follows: diethyl ether and n-butyl ethyl ether: < 5 min, di-*i*-propyl

ether[11] and *t*-butyl methyl ether: 3/4 h, and *t*-butyl ethyl ether: > 24 h at 50 °C. With asymmetrically substituted ethers, *t*-butyl methyl ether, *t*-butyl ethyl ether and *n*-butyl ethyl ether the selectivity of C-O activation by **1a** was studied and remarkable differences were observed. Reaction of **1a** with t-butyl methyl ether was studied before and gave selectively Cp^*_2YOMe (**4**).[11] With *t*-butyl ethyl ether a 1 : 1 mixture of **2a** and $Cp^*_2YO^tBu$ (**5a**) was obtained. Complete conversion took 4 d at 50 °C. When *t*-butyl ethyl ether was added in a ratio Y : ^{t}BuOEt = 1 : 5, reaction was complete within 14 h at room temperature yielding the same product ratio. There were no signs of complexation of *t*-butyl ethyl ether either to the products Cp^*_2LnOR or to the starting compound **1a**, which is probably a consequence of the high steric requirements of the ether. With *n*-butyl ethyl ether the C-O activation process became selective again, leading to quantitative formation of **6a** and ethane. Analogous to the reaction with diethyl ether, there were resonances present in the ^{1}H-NMR spectrum which were assigned to an intermediate ether adduct $Cp^*_2YD(^n$BuOEt).

Table I. Results of the Ether Cleavage Reactions with $(Cp^*_2LnH)_2$.

$(Cp^*_2LnH)_2$	ROR'	Cp^*_2LnOR, Cp^*_2LnOR'
1a	Et_2O	**2a** Cp^*_2YOEt
1b	Et_2O	**3b** $Cp^*_2LaOEt(Et_2O)$
1c	Et_2O	**3c** $Cp^*_2CeOEt(Et_2O)$
1a	^{t}BuOMe	**4** Cp^*_2YOMe[11]
1a	^{t}BuOEt	**2a** Cp^*_2YOEt
		5a $Cp^*_2YO^tBu$ (1 : 1)
1a	^{n}BuOEt	**6a** $Cp^*_2YO^nBu$
1b	^{t}BuOEt	**2b** Cp^*_2LaOEt
		5b $Cp^*_2LaO^tBu$ (2 : 3)
1b	^{n}BuOEt	**6b** $Cp^*_2LaO^nBu(^n$BuOEt)

To understand better the mechanism of C-O activation, the kinetics of the cleavage of Et_2O by **1a** were determined by ^{1}H-NMR under pseudo first order conditions in Et_2O. It was found that at 0 °C, $Cp^*_2YH(Et_2O)$ (**7**) was the only species present immediately after addition of Et_2O. The monomeric identity of this compound is without question since the signal observed in the ^{1}H-NMR for the hydride ligand (δ = 5.62 ppm) appears as a doublet due to coupling with one

yttrium nucleus ($^1J_{HY}$ = 83.1 Hz). This hydride species reacted quantitatively to **3a** and ethane with a first order dependence in [$Cp^*_2YH(Et_2O)$] at 0 °C for more than 5 half-lives ([**1a**]$_0$ = 0.026 M, [Et_2O]$_0$ = 0.25 M, k_{obs} = 7.4 ± 0.1 · 10^{-4} s^{-1}; [**1a**]$_0$ = 0.12 M, [Et_2O]$_0$ = 1.21 M, k_{obs} = 6.7 ± 0.1 · 10^{-4} s^{-1}). This shows that the actual C-O activation involves dissociation of dimeric **1a** to form **7**, which then intramolecularly converts to products.

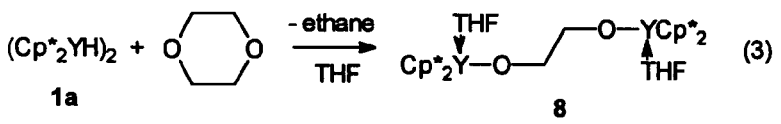
To study the influence of increased ionic radius of the Ln center on C-O activation, reactions of aliphatic ethers with **1b** were performed. The reactivity order diethyl ether ≈ *n*-butyl ethyl ether >> *t*-butyl ethyl ether is in good agreement with the one found for **1a**. The rate of reaction with *t*-butyl ethyl ether was much higher than with **1a**, however (2 h vs 14 h at room temperature, 5 fold excess of ^{t}BuOEt). The selectivity pattern found for cleavage of *t*-butyl ethyl ether and *n*-butyl ethyl ether is very similar to the one found for **1a** (Table I). For *t*-butyl ethyl ether a 2 : 3 ratio of Cp^*_2LaOEt (**2b**) and $Cp^*_2LaO^tBu$ (**5b**) was found which differs slightly from the corresponding reaction for **1a**. Since no dramatic difference between Ln = Y and La was found, from this point onward we only studied hydride **1a** for convenience.

Cyclic ethers gave as anticipated ring opening when allowed to react with **1a**. With THF initially the THF adduct $Cp^*_2YH(THF)$ was formed, which subsequently converted to a mixture of products (24 h at room temperature) of which **6a** could be identified as the major component (60 % by ^{1}H-NMR, eq 2).[13] In benzene-d_6 the reaction appeared to be more complicated due to H/D scrambling between the hydride, the α-methylene hydrogen atoms of THF and the solvent,[11] but apart from this, no indications were obtained for a different reactivity.

$$(Cp^*_2YH)_2 \xrightarrow{THF} Cp^*_2YH(THF) \longrightarrow Cp^*_2YO^nBu \quad (2)$$

1a **6a**

1,4-Dioxane and **1a** reacted to give a white precipitate which was recrystallized from THF and identified as the bimetallic glycolate complex $(Cp^*_2Y)_2(\mu\text{-}OCH_2CH_2O)(THF)_2$ (**8**) (eq. 3). The gas evolved was collected by Töpler pump and analyzed as ethane (0.50 mol/mol Y, GC).[14] When the reaction was monitored by ^{1}H-NMR it became clear that the product was formed practically instantaneously.



1a

8

The ^{1}H- and ^{13}C-NMR spectra of **8** show one resonance for all Cp* ligands. For the methylene groups in the OCH_2CH_2O bridge also one resonance is observed in both the ^{1}H- and ^{13}C-NMR. This methylene resonance appears as a doublet in the ^{1}H-decoupled ^{13}C-NMR spectrum due to a $^2J_{CY}$ coupling of 5 Hz. These data suggest a structure with either a two fold rotation axis or an inversion center. A dynamic process, which is fast on the NMR time scale, might also account for the observed equivalence of the Cp* and OCH_2 groups. A structure that places the oxygen atoms of the OCH_2CH_2O bridge in bridging positions between two yttrium centers can be excluded because each OCH_2 group is coupled to only one yttrium nucleus.

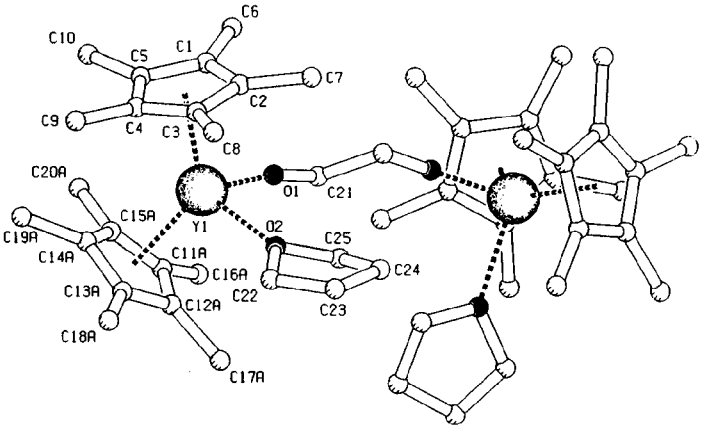


Figure 1. *PLUTON* drawing of $(Cp^*_2Y)_2(\mu\text{-}OCH_2CH_2O)(THF)_2$ (**8**).

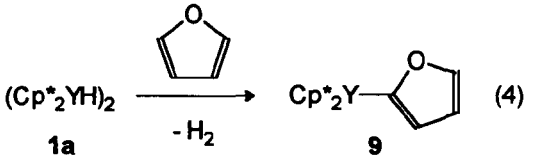
To elucidate the bonding of the glycolate ligand in **8**, a single-crystal X-ray structure determination was undertaken. A *PLUTON* diagram of the resulting molecular structure is shown in Figure 1. Selected bond distances and angles are listed in Table II. The molecule is situated on a crystallographic 2-fold symmetry axis, which is in agreement with the NMR data. The molecule consists of two

$Cp^*_2Y(THF)$ units, which have a distorted tetrahedral arrangement and which are bridged by the glycolate ligand. The bonding of THF and the Cp* ligands to yttrium is normal. The Y1-O1 distance compares well with those in alkoxides $Cp^*Y(OC_6H_3{}^tBu_2)_2$ (2.096(4) and 2.059(3))[15] and $[Cp^*Y(\mu\text{-}O^tBu)(O^tBu)]_2$ (1.995(10) and 2.018(9)).[16] Also the almost linear Y1-O1-C21 angle due to π-overlap of the oxygen lone pairs with metal orbitals has been observed in $Cp^*Y(OC_6H_3{}^tBu_2)_2$.[15]

Table II. Selected Bond Distances (Å) and Angles (°) for $(Cp^*_2Y)_2(\mu\text{-}OCH_2CH_2O)(THF)_2$ (8).

Y1-O1	2.042(4)	O1-C21	1.359(9)
Y1-O2	2.398(5)	C21-C21a	1.484(9)
O1-Y1-O2	89.54(16)	O1-C21-C21a	116.0(7)
Y1-O1-C21	168.2(4)	O1-C21-C21a-O1a	163.1(6)

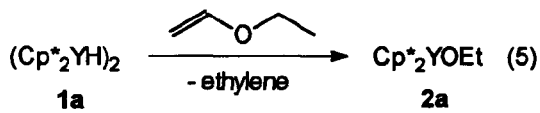
As opposed to THF and 1,4-dioxane, furan was not ring opened by **1a**. Instead C-H activation of furan in the α-position to form $Cp^*_2Y(2\text{-}OC_4H_3)$ (**9**) was observed (^{1}H-NMR, eq 4). This compound was characterized as the bis THF adduct $Cp^*_2Y(2\text{-}OC_4H_3)(THF)_2$ (**10**) which could be prepared independently from $Cp^*_2YCl_2Li(Et_2O)_2$ and 2-lithiofuran.



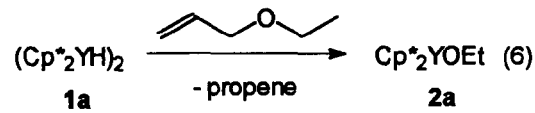
(4)

C-O activation in the unsaturated ethers vinyl ethyl ether and allyl ethyl ether was found to be very rapid ($t_{1/2}$ < 2 min). With vinyl ethyl ether a rapid reaction producing **2a** in essentially quantitative yield was observed (eq. 5). Only a minor amount of gas was collected by Töpler pump (0.05 mol ethylene/mol Y, GC). The fate of the missing CH_2CH_2 fragments was determined by GC/MS after the reaction mixture had been quenched with methanol. The mixture contained higher alkanes in the range C16 to C22 with exclusively even numbers of carbon atoms. This

indicates that the ethylene evolved is oligomerized under the reaction conditions applied. This is most likely caused by reaction with **1a** which is an active ethylene polymerization catalyst.[17] Attempts to observe an intermediate at -80 °C were unsuccessful (^{1}H-NMR). The yttrium hydride **1a** had already been converted to **2a** when a solution of **1a** in toluene-d_8, to which vinyl ethyl ether had been added at -196 °C, was warmed to -80 °C.

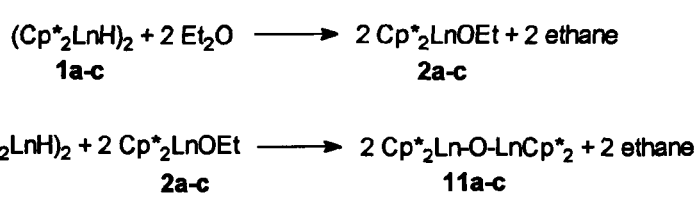


With allyl ethyl ether again the main product formed was **1a** (57 % by ^{1}H-NMR, eq 6). The gas evolved (0.56 mol/mol Y) was analyzed as a mixture of propene (79 %) and propane (21 %) by GC.



Attempted hydrogenation of vinyl ethyl ether under mild conditions was carried out with a ten fold excess of vinyl ethyl ether (p = 1 bar, room temperature). This led to quantitative formation of the vinylether adduct of **2a**. Hydrogenation to diethyl ether was not observed, however. Also attempted hydrogenation of allyl ethyl ether led to fast formation of the allyl ethyl ether adduct of **2a** and no hydrogenation product was observed.

Scheme I



C-O Cleavage in Alkoxides Cp*$_2$LnOR. Not only ethers are activated by hydrides **1a-c** but even the C-O bonds of alkoxides Cp*$_2$LnOEt (Ln = Y, La, Ce

(**2a-c**)) are attacked, leading to bimetallic complexes $(Cp^*_2Ln)_2(\mu\text{-}O)$ (Ln = Y, La, Ce (**11a-c**), Scheme I). When diethyl ether was added to a solution of **1a** in a 1 : 1 ratio, the diethyl ether was completely converted to **2a** and ethane within a few minutes (^{1}H-NMR). The excess **1a** was still present then. At 80 °C, **1a** reacted in about 4 days with **2a** to form **11a** and ethane. In a preparative experiment, 0.49 mol ethane/per mol Y was collected after 0.5 h at room temperature. After 4 days at 80 °C another 0.47 mol ethane/per mol Y was collected. This is in agreement with the two step reaction sequence depicted in Scheme I and the NMR experiment. Crystallization from THF afforded unsolvated **11a** as white crystals.

Reactions of **1b** and **1c** with diethyl ether to form **11b** and **11c** proceeded analogously (^{1}H-NMR). For cerium the molecular structure of $(Cp^*_2Ce)_2(\mu\text{-}O)(THF)_2$ has been determined by X-ray crystallography.[18]

Activation of Sulfides. In contrast to ethers, organic sulfides are activated predominantly by C-H activation to form the corresponding metallation products. Reaction of **1a** with Me_2S led to formation of $Cp^*_2YCH_2SMe$ (**12**) (eq 7). The product could be isolated as the THF adduct $Cp^*_2YCH_2SMe(THF)$ (**13**) in reasonable yield. NMR tube experiments revealed that the reaction is very rapid at room temperature and essentially quantitative with excess Me_2S. When smaller amounts of Me_2S are used (Me_2S : Y ≤ 1) formation of an unidentified product, resulting from consecutive reaction of **12** with **1a**, was observed.[19]

$$\underset{\textbf{1a}}{(Cp^*_2YH)_2} \xrightarrow[-H_2]{Me_2S} \underset{\textbf{12}}{Cp^*_2YCH_2SMe} \qquad (7)$$

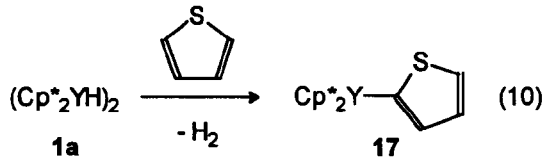
Metallation was also observed with benzyl methyl sulfide and $Cp^*_2YC(H)(SMe)Ph$ (**14**) was obtained (eq 8). However Et_2S, in contrast to dimethyl sulfide and benzyl methyl sulfide, was not metallated but underwent C-S cleavage instead. No signs for C-H activation of Et_2S were present (^{1}H-NMR) and clean formation of Cp^*_2YSEt (**15**) was observed (eq 9). The product was isolated and identified as the THF adduct $Cp^*_2YSEt(THF)$ (**16**).

$$\underset{\textbf{1a}}{(Cp^*_2YH)_2} \xrightarrow[-H_2]{PhCH_2SMe} \underset{\textbf{14}}{Cp^*_2Y(SMe)(Ph)} \qquad (8)$$

$$(Cp^*_2YH)_2 \xrightarrow[-\text{ethane}]{Et_2S} Cp^*_2YSEt \quad (9)$$

1a **15**

Thiophene behaves analogously to furan, dimethyl sulfide and benzyl methyl sulfide and was metallated selectively in the α-position to form $Cp^*_2Y(2\text{-}SC_4H_3)$ (**17**) (eq 10). The product could be isolated in high yield as the THF adduct $Cp^*_2Y(2\text{-}SC_4H_3)(THF)$ (**18**).



Allyl methyl sulfide was studied to examine whether activation took place at the C-S, C=C or C-H bonds. ^{1}H-NMR studies showed the complete conversion of **1a** to a mixture of compounds within several minutes at room temperature. A doublet of triplets ($^3J_{HH}$ = 7.1 Hz, $^2J_{HY}$ = 3.7 Hz) at δ = -0.30 ppm and a triplet at δ = 2.66 ppm ($^3J_{HH}$ = 6.8 Hz) in the ^{1}H-NMR spectrum were assigned to YCH_2CH_2 and CH_2S moieties respectively. From this and the presence of a Cp* resonance (δ = 1.91 ppm) we concluded that the insertion product $Cp^*_2YCH_2CH_2CH_2SMe$ (**19**) was formed in 53 % yield.[20]

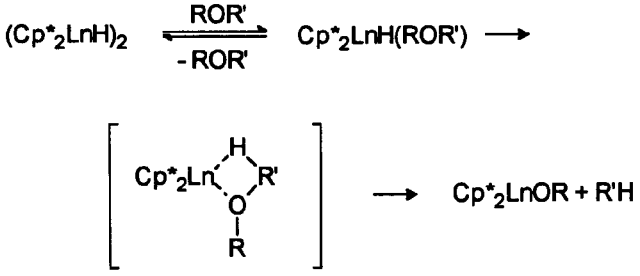
No polymerization was observed with excess allyl methyl sulfide (NMR, GC) which is probably due to shielding of the metal center by the internal coordination of the SMe group. However, under H_2 atmosphere (1 bar) it was possible to hydrogenate catalytically allyl methyl sulfide to *n*-propyl methyl sulfide in moderate yield (30 %).

Discussion

In analogy with C-H activation reactions, C-O activation by Lewis acidic lanthanide complexes, $(Cp^*_2LnH)_2$ (Ln = Sm,[21] Lu[22]), has been explained in terms of σ-bond metathesis[1a,23] (Scheme II). First the ether molecule is coordinated to the hydride complex forming monomeric $Cp^*_2LnH(R_2O)$ which makes the α-C atom of

the ether molecule susceptible to nucleophilic attack by the hydride ligand in the second step. Our observations for Y, La and Ce are in good agreement with the results for Sm and Lu, emphasizing the strong similarities between group 3 metals and lanthanides. For yttrium, the intermediate ether hydride adducts $Cp^*_2LnH(ROR')$ and $Cp^*_2YD(ROR')$ were observed by ^1H-NMR which supports the proposed dissociation of dimeric $(Cp^*_2LnH)_2$ in the first step of Scheme II. This is confirmed by the observed first order dependence in [7].

Scheme II



The reactivity order diethyl ether ≈ *n*-butyl ethyl ether > di-*i*-propyl ether ≈ *t*-butyl methyl ether > *t*-butyl ethyl ether reflects the increasing steric requirements of the ethers involved. Approach and complexation of ether to $(Cp^*_2LnH)_2$ becomes more difficult with increasing steric bulk on the ether molecule. This is in line with the fact that monomeric ether adducts $Cp^*_2YH(R_2O)$ and $Cp^*_2YD(R_2O)$ could only be observed for the less bulkier ethers (Et_2O, ^{n}BuOEt and THF). The observation that the bulkiest ether, *t*-butyl ethyl ether, reacts slightly faster with **1b** than with **1a** can be explained by the fact that La has a larger ionic radius than Y[24] which makes complexation of the ether molecule more favorable.

For aliphatic nucleophilic substitution reactions it is well-known that alkyl substituents on the α-C atom of the substrate RX can have an enormous effect on reactivity.[25] In S_N2 type substitution, the reactivity order for different R is: Me > Et > Pr >> Np > Bu whereas for S_N1 substitution the order Bz ≈ allyl > 3° > 2° > 1° > Me is observed. In S_N2 substitution the reactivity is governed by steric characteristics of R, whereas in S_N1 substitution the stabilisation of a positive charge on the α-C atom is of dominating importance. Ether cleavage of the S_N2 type has been observed with hydrohalic acids (HX) proceeding by S_N2 attack of X^-

on the less hindered C-O bond.[26] Ether cleavage by strong Lewis acids like boron trihalogenides is an example of a S_N1 type mechanism.[26]

Our systems show similarities with both of these nucleophilic aliphatic substitution reactions. The observation that *t*-butyl methyl ether is attacked at the more substituted α-C atom indicates that electronic rather than steric factors are important and suggests an S_N1 mechanism. However, from reaction of *t*-butyl ethyl ether, in which both C-O bonds are cleaved at comparable rates, and from reaction of *n*-butyl ethyl ether, which is cleaved at the Et-O bond, it is clear that steric requirements of the ether molecules are important as well.

Only an insignificant effect on the selectivity of ether splitting is found when the results for **1a** are compared with those for **1b**, although the ionic radii of Y and La are very different.[24] From this it is concluded that steric and electronic characteristics of the ether itself and not those of the $(Cp^*_2LnH)_2$ system determine the selectivity of the ether splitting.

The ring opening observed with 1,4-dioxane and THF fits well within the σ-bond metathesis scheme described above. Ring opening of THF has also been reported for $(Cp^*_2SmH)_2$.[21] With 1,4-dioxane the first step is most likely formation of $Cp^*_2YOCH_2CH_2OEt$. Formation of **8** requires the selective cleavage of the O-Et bond in the second step.

The complete deoxygenation of ethers by nucleophilic metal hydride complexes is to our knowledge without precedent. There have been some reports however concerning formation of μ-oxo species which might be attributed to the deoxygenation of THF. For instance $Cp^*_2Sm(\mu\text{-}O)SmCp^*_2$ was obtained as a side product in the ringopening of THF by $(Cp^*_2SmH)_2$.[21] Another example is the isolation of $Cp_2Lu(THF)(\mu\text{-}O)(THF)LuCp_2$ from attempted crystallization of $Cp_2LuAsPh_2(THF)$ from THF, which was explained by hydrolysis due to traces of water.[27] A plausible explanation is that the μ-oxo ligand originates from double C-O cleavage of THF. This explanation is even more likely when the ring opening of THF by $Cp_2LuPPh_2(THF)$, leading to $Cp_2LuO(CH_2)_4PPh_2$, is considered.[27] The slower formation of the μ-oxo species for Y compared to La and Ce can be understood on the basis of the smaller ionic radius of Y.[24] Attack on the C-O bond of the alkoxide to reach a four-centered transition state will be easier for La and Ce as a result of the larger coordination sphere of these metal ions.

The C-O activation of vinyl ethyl ether does not necessarily have to follow the same route as proposed in scheme II. An alternative mechanism involving insertion of the double bond into the Y-H bond followed by β-alkoxide elimination and

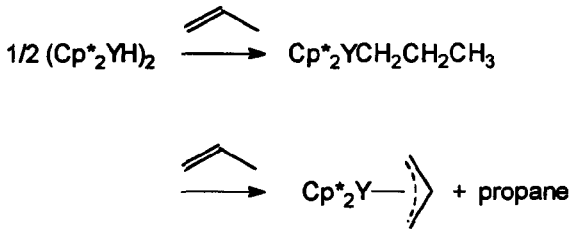
evolution of ethylene can not be ruled out *a priori*. Insertion might also play an important role in the reaction of allyl ethyl ether. However, attempts to observe an insertion product were unsuccessful.

The fast formation of ethoxide **2a** also kills the polymerization and hydrogenation activity of **1a** since no hydrogenation or polymerization products of vinyl ethyl ether and allyl ethyl ether were observed. This is in remarkable contrast to the very high activity of $(Cp^*_2LnH)_2$ systems in hydrogenation[2] and polymerization[1] of non-functionalized olefins.

The formation of propene in the cleavage of allyl ethyl ether by **1a** is most likely the result of direct attack on the allyl-O bond although a 6-membered transition state has also been suggested for C-O activation in allyl ethers.[8] A plausible explanation for the formation of propane is allylic C-H activation of propene and $Cp^*_2Ln(\eta^3$-allyl) which is well-known for Cp^*_2LnR complexes (Ln = Y,[17] Lu,[1b] La, Nd,[1]). The propene formed by C-O activation of allyl ethyl ether reacts with **1a** to form $Cp^*_2YCH_2CH_2CH_3$ (Scheme III). Next propane and $Cp^*_2Y(\eta^3$-allyl) are formed by reaction of $Cp^*_2YCH_2CH_2CH_3$ with propene. Attempts to observe $Cp^*_2Y(\eta^3$-allyl) in the ^{1}H-NMR spectrum were frustrated by overlap with resonances of unidentified material.

As has been shown by Marks and co-workers[28] the driving force for the cleavage of C-X bonds is undoubtedly the formation of very stable Ln-X bonds. The overall reaction enthalpies ($\Delta H°$) of C-X cleavage in ethers and sulfides with $(Cp^*_2SmH)_2$ were calculated to be -48 kcal/mol (Me_2O) and -53 kcal/mol (Me_2S) respectively. These values are significantly more exothermic than for C-H activation of hydrocarbons. For instance the reaction enthalpy for metallation of benzene by Cp^*_2ScH was determined to be slightly endothermic by +6.7(3) kcal/mol.[1a]

Scheme III



From this it follows that C-X activation would be the thermodynamically favored process. However the observed metallation of RX suggests that kinetic parameters are important as well. Both from experimental and theoretical work it has become clear that σ-bond metathesis is strongly dependent on steric requirements in the transition states. It was found that metallations of hydrocarbons by $(Cp^*_2LnH)_2$ have low activation energies.[23b,c,29] Especially increasing substitution on the atoms participating in the four-centered transition state leads to a dramatic increase in activation energy. Since for C-H activation there are two hydrogens participating in the four-centered transition state whereas for C-X activation only one hydrogen is involved (Figure 2), the steric requirements for C-H activation are expected to be less than for C-X activation. This could explain why, although the thermochemistry for both processes is very different, competition between C-H and C-X activation is possible. In addition this effect can be enhanced by the increased acidity of the α-H's compared to hydrogens of hydrocarbons.

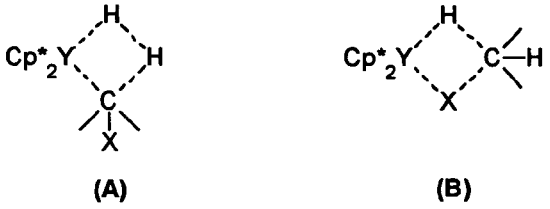


Figure 2. Transition states for C-H (A) and C-X activation (B).

When comparing the activation of ethers and sulfides it is clear that C-X cleavage is more facile for ethers than for sulfides which could be the result of the lower BDE's of Ln-SR bonds vs Ln-OR bonds and the lower electronegativity of S vs O.[28] The result is that C-H activation and formation of metallated species can compete better. The observation of the insertion product and the modest hydrogenation activity with allyl methyl sulfide also indicate that deactivation is less important compared to unsaturated ethers.

Conclusions

It was shown that C-O cleavage of ethers with $(Cp^*_2LnH)_2$ complexes has a broad scope. Only furan was found to react differently because of the facile ortho C-H activation pathway available. The cleavage pattern observed with asymmetric substituted ethers can be explained by a σ-bond metathesis mechanism and in some cases very selective cleavages can be achieved. The unique activation of alkoxide C-O bonds by $(Cp^*_2LnH)_2$ complexes is a good synthetic route to bimetallic $(Cp^*_2Ln)_2(\mu\text{-}O)$ complexes. As a consequence of the facile formation of alkoxides and oxides, molecules containing ether functionalities give very fast deactivation of the catalyst in hydrogenation and polymerization. For sulfides C-S cleavage is less favorable and C-H activation can compete more effectively allowing the formation of interesting metallation products. Hydrogenation of allyl methyl sulfide in moderate yield shows that deactivation of organolanthanide catalysts by C-X activation is less important for sulfide functionalities in the substrate molecule.

Experimental Section

General Considerations. All experiments were performed under nitrogen using standard Schlenk, glovebox (Braun MB200), and vacuum line techniques. Et_2O, pentane, THF, cyclohexane, benzene, benzene-d_6, toluene-d_8, and THF-d_8 were distilled from Na/K alloy and degassed prior to use. Compounds **1a-c**,[30,1e,31] $Cp^*_2YCl(LiCl)(Et_2O)_2$,[32] 2-lithiofuran[33] and ^{t}BuOEt[26] were prepared according to published procedures. H_2 (99.9995%, Hoek-Loos) was used without further purification. ^{t}BuOEt, ^{n}BuOEt, vinyl ethyl ether and allyl ethyl ether were distilled twice from Na sand. Other reagents and cyclohexane-d_{12} were stored over mol sieves (4 Å). NMR spectra were recorded on Bruker WH90 (^{1}H: 90 MHz), Gemini 200 (^{1}H: 200 MHz) and Varian VXR-300 (^{1}H: 300 MHz, ^{13}C: 75.4 MHz) spectrometers at ambient temperatures. GC analyses were carried out on a Hewlett Packard HP5890-A instrument equiped with a Hewlett Packard HP 3390 integrator using Porapack Q and Porasil B columns. GC/MS analyses were carried out on a Ribermag R 10-10 C instrument using a CP Sil 5 CB column and MS spectra were recorded on a AEI MS 902 mass spectrometer. IR spectra were recorded as Nujol mulls between KBr disks on a Mattson Instruments Galaxy-4020 FT-IR spectrophotometer. Elemental analyses were carried out at the Micro-Analytical

Department of the University of Groningen. The determinations are the average of at least two independent determinations.

NMR Tube Reaction of $(Cp^*_2YH)_2$ (1a) with Et_2O. In an NMR tube 0.020 g (0.028 mmol) of **1a** was dissolved in a mixture of 5.8 μL (0.056 mmol) Et_2O and 0.5 mL of benzene-d_6. ^{1}H-NMR after 10 min at room temperature showed the formation of $Cp^*_2YD(Et_2O)$, and **2a** (1 : 3). After 20 min at room temperature, ^{1}H-NMR showed the formation of **2a** (100 %) and ethane (δ = 0.79 ppm). ^{1}H-NMR of **2a** (300 MHz, benzene-d_6): δ 4.28 (q, $^3J_{HH}$ = 6.9 Hz, 2H, OCH_2CH_3), 1.93 (s, 30H, C_5Me_5), 1.31 (t, $^3J_{HH}$ = 6.9 Hz, 3H, OCH_2CH_3). ^{13}C-NMR of **2a** (75.4 MHz, benzene-d_6): δ 118.01 (s, C_5Me_5), 62.10 (td, $^1J_{CH}$ = 136 Hz, $^2J_{CY}$ = 6 Hz, OCH_2CH_3), 22.40 (q, $^1J_{CH}$ = 123 Hz, OCH_2CH_3), 10.53 (q, $^1J_{CH}$ = 124 Hz, C_5Me_5). ^{1}H-NMR of $Cp^*_2YD(Et_2O)$ (300 MHz, benzene-d_6): δ 3.37 (q, $^3J_{HH}$ = 7.0 Hz, 4H, OCH_2CH_3), 2.08 (s, 30H, C_5Me_5), 0.84 (t, $^3J_{HH}$ = 7.0 Hz, 6H, OCH_2CH_3).

Kinetic Measurements. NMR tubes (5 mm with Young valve) were filled with solutions of **1a** in methylcyclohexane-d_{14} of accurately determined concentration. At -196 °C known amounts of Et_2O were added and the NMR tubes were sealed under nitrogen atmosphere. The reaction mixtures were allowed to become homogeneous at -30 °C and were quickly inserted in the probe of an NMR spectrometer and warmed to 0 °C. The progress of the reaction was monitored by taking a ^{1}H-NMR spectrum (300 MHz) at constant intervals (at least 3 spectra per half-live) for more than 5 half-lives. The decrease in intensity of the Cp* and YH signals of **7** were fitted to an exponential decay using a least-squares method. At the end of the measurement it was checked that no insoluble material was present. ^{1}H-NMR of **7** (300 MHz, methylcyclohexane-d_{12}): δ 5.62 (d, $^1J_{HY}$ = 83.1 Hz, 1H, YH), 1.92 (s, 30H, C_5Me_5).

NMR Tube Reaction of $(Cp^*_2LaH)_2$ (1b) with Et_2O. In an NMR tube 0.020 g (0.025 mmol) of **1b** was dissolved in 0.5 mL of benzene-d_6 and 16 μL (0.16 mmol) of Et_2O was added. ^{1}H-NMR after 10 min at room temperature showed the quantitative formation of **3b** and ethane (δ = 0.78 ppm). The NMR tube was opened and volatiles were removed in vacuum. The residue was redissolved in benzene-d_6. ^{1}H-NMR (300 MHz, benzene-d_6): δ 4.15 (q, $^3J_{HH}$ = 6.8 Hz, 2H, $LaOCH_2CH_3$), 3.28 (q, $^3J_{HH}$ = 7.3 Hz, 4H, $O(CH_2CH_3)_2$), 2.08 (s, 30H, C_5Me_5),

1.27 (t, $^3J_{HH}$ = 6.8 Hz, 3H, $LaOCH_2CH_3$), 0.87 (t, $^3J_{HH}$ = 7.3 Hz, 6H, $O(CH_2CH_3)_2$.

NMR Tube Reaction of 1a with ^{t}BuOEt. In an NMR tube 0.020 g (0.028 mmol) of **1a** was dissolved in a mixture of 7.6 μL (0.056 mmol) of ^{t}BuOEt and 0.5 mL of benzene-d_6. ^{1}H-NMR showed the formation of a mixture of **2a** (49 %) and **5a** (43 %) together with a small amount of unidentified material (8 %) over a period of 4 d at 50 °C. Resonances expected for isobutane (doublet at δ = 0.85 ppm) and ethane (δ = 0.78 ppm) were also observed. ^{1}H-NMR for **5a** (300 MHz, benzene-d_6): δ 1.95 (s, 30H, C_5Me_5) 1.41 (s, 9H, ^{t}Bu). ^{13}C-NMR (75.4 MHz, benzene-d_6): δ 118.36 (s, C_5Me_5), 72.50 (d, $^2J_{CY}$ = 6 Hz, CMe_3), 35.20 (qsept, $^1J_{CH}$ = 124 Hz, $^3J_{CH}$ = 4 Hz, CMe_3), 11.30 (q, $^1J_{CH}$ = 125 Hz, C_5Me_5).

NMR Tube Reaction of 1a with ^{n}BuOEt. In an NMR tube 0.021 g (0.029 mmol) of **1a** was dissolved in a mixture of 7.7 μL (0.056 mmol) of ^{n}BuOEt and 0.5 mL of benzene-d_6. ^{1}H-NMR after 15 min at room temperature showed the formation of **6a** and resonances which were assigned to $Cp^*_2YD(^n$BuOEt) (3 : 1). After 1 h at room temperature quantitative conversion to **6a** and ethane (δ = 0.78 ppm) had taken place. ^{1}H-NMR for **6a** (300 MHz, benzene-d_6): δ 4.23 (t, $^3J_{HH}$ = 7.0 Hz, 2H, OCH_2), 1.95 (s, 30 H, C_5Me_5), 1.68 (quint, $^3J_{HH}$ = 7.3 Hz, 2H, $YOCH_2CH_2$), 1.43 (sext, $^3J_{HH}$ = 7.3 Hz, 2H, $CH_2CH_2CH_3$), 1.05 (t, $^3J_{HH}$ = 7.3 Hz, 3H, $CH_2CH_2CH_3$). ^{13}C-NMR (75.4 MHz, benzene-d_6): δ 117.86 (s, C_5Me_5), 67.24 (td, $^1J_{CH}$ = 135 Hz, $^2J_{CY}$ = 7 Hz, $YOCH_2$), 39.20 (t, $^1J_{CH}$ = 121 Hz, $YOCH_2CH_2$), 19.85 (t, $^1J_{CH}$ = 122 Hz, $CH_2CH_2CH_3$), 14.73 (q, $^1J_{CH}$ = 124 Hz, $CH_2CH_2CH_3$), 10.70 (q, $^1J_{CH}$ = 125 Hz, C_5Me_5).

NMR Tube Reaction of 1b with ^{t}BuOEt. In an NMR tube 0.014 g (0.017 mmol) of **1b** was dissolved in 0.5 mL of benzene-d_6 and 25 μL (0.18 mmol) of ^{t}BuOEt was added. ^{1}H-NMR showed that a mixture of **2b** (44 %) and **5b** (56 %) had been formed within 2 hours at room temperature. Also resonances of isobutane (doublet at δ = 0.85 ppm) and ethane (δ = 0.79 ppm) were observed. The NMR tube was opened and volatiles were removed in vacuum. The residue was redissolved in benzene-d_6. ^{1}H-NMR (300 MHz, benzene-d_6): δ 3.95 (q, $^3J_{HH}$ = 7.3 Hz, 2H, $LaOCH_2CH_3$), 1.97 (s, overlapping C_5Me_5 resonances of Cp^*_2LaOEt and $Cp^*_2LaO^tBu$), 1.38 (s, 9H, ^{t}Bu), 1.25 (t, $^3J_{HH}$ = 7.3 Hz, 3H, $LaOCH_2CH_3$).

NMR Tube Reaction of 1b with ^{n}BuOEt. In an NMR tube 0.016 g (0.019 mmol) of **1b** was dissolved in 0.5 mL of benzene-d_6 and 25 μL (0.18 mmol) of ^{n}BuOEt was added. ^{1}H-NMR after 10 min at room temperature showed that **6b** had been formed in 87 % yield. Volatiles were removed in vacuo and the residue was redissolved in benzene-d_6. ^{1}H-NMR (300 MHz, benzene-d_6): δ 4.11 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $LaOCH_2$), 3.30 (m, 4H, ^{n}BuOEt), 2.10 (s, 30H, C_5Me_5), 1.67 (quint, $^3J_{HH}$ = 7.3 Hz, 2H, $LaOCH_2CH_2$), 1.44 (m, 4H, $LaO(CH_2)_2CH_2CH_3$ and ^{n}BuOEt), 1.13 (sext, $^3J_{HH}$ = 7.3 Hz, 2H, ^{n}BuOEt), 1.04 (t, $^3J_{HH}$ = 7.3 Hz, 3H, $LaO(CH_2)_3CH_3$), 0.96 (t, $^3J_{HH}$ = 7.3 Hz, 3H, ^{n}BuOEt), 0.84 (t, $^3J_{HH}$ = 7.3 Hz, 3H, ^{n}BuOEt). ^{13}C-NMR (75.4 MHz, benzene-d_6): δ 117.83 (s, C_5Me_5), 70.69, (t, $^1J_{CH}$ = 141 Hz, OCH_2 of ^{n}BuOEt), 68.00 (t, $^1J_{CH}$ = 135 Hz, $LaOCH_2$), 66.65 (t, $^1J_{CH}$ = 142 Hz, OCH_2 of ^{n}BuOEt), 39.30 (t, $^1J_{CH}$ = 124 Hz, $LaOCH_2CH_2CH_2Me$), 31.17 (t, $^1J_{CH}$ = 124 Hz, CH_2 of ^{n}BuOEt), 19.91 (t, $^1J_{CH}$ = 123 Hz, $LaO(CH_2)_2CH_2Me$), 19.14 (t, $^1J_{CH}$ = 123 Hz, Me of ^{n}BuOEt), 14.69 (q, $^1J_{CH}$ = 126 Hz, $LaO(CH_2)_3Me$), 14.58 (q, $^1J_{CH}$ = 126 Hz, Me of ^{n}BuOEt), 14.00 (q, $^1J_{CH}$ = 124 Hz, Me of ^{n}BuOEt), 11.28 (q, $^1J_{CH}$ = 124 Hz, C_5Me_5).

NMR Tube Reaction of 1a with THF. In an NMR tube 4.9 μL (0.060 mmol) of THF was added to a solution of 0.021 g (0.028 mmol) of **1a** in 0.5 ml of cyclohexane-d_{12}. ^{1}H-NMR after 10 min at room temperature showed the clean formation of $Cp^*_2YH(THF)$ which upon warming to 85 °C converted to **6a** (^{1}H- and ^{13}C-NMR, 60 %) within 1 h along with some unidentified products. ^{1}H-NMR of $Cp^*_2YH(THF)$ (90 MHz, cyclohexane-d_{12}): δ 5.70 (d, $^1J_{HY}$ = 78 Hz, $\Delta\nu_{1/2}$ = 14 Hz, 1H, YH), 3.84 (m, 4H, α-THF), 1.94 (s, 30H, C_5Me_5), 1.88 (m, 4H, β-THF). ^{1}H-NMR of **6a** (300 MHz, cyclohexane-d_{12}): δ 3.98 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $YOCH_2$), 1.91 (s, 30H, C_5Me_5), 1.48 (quint, $^3J_{HH}$ = 7.3 Hz, 2H, OCH_2CH_2), 1.28 (sext, $^3J_{HH}$ = 7.3 Hz, 2H, $O(CH_2)_2CH_2$), 0.92 (t, $^3J_{HH}$ = 7.3 Hz, 3H, $O(CH_2)_3Me$).

$(Cp^*_2Y)_2(\mu\text{-}OCH_2CH_2O)(THF)_2$ (8). On a vacuum line, a bulb containing 0.242 g (0.336 mmol) of **1a** was evacuated. A mixture of 58 μL (0.68 mmol) of 1,4-dioxane and 5.0 ml of toluene was condensed on the solid at -196 °C. The reaction mixture was allowed to warm to room temperature and stirred for 15 hours. A white precipitate was formed. The gasses evolved were collected by Töpler pump and analyzed by GC to be ethane (0.34 mmol, 0.50 mol/mol Y). Volatiles were removed in vacuum and the white solid was redissolved in 10 mL of

THF. Crystallization at -80 °C yielded 0.184 g (0.20 mmol, 59 %) of **8** as white crystals. IR (cm^{-1}) 2900 (s), 2799 (sh), 2724 (m), 2658 (m), 2562 (w), 1462 (s), 1379 (s), 1314 (m), 1294 (m), 1273 (m), 1134 (vs), 1074 (m), 1061 (m), 1020 (s), 914 (m), 872 (s), 802 (w), 723 (m), 669 (w), 635 (vw), 590 (w), 421 (s). ^{1}H-NMR (300 MHz, THF-d_8): δ 3.90 (s, 4H, $YOCH_2CH_2OY$), 1.88 (s, 60H, C_5Me_5). ^{13}C-NMR (75.4 MHz, THF-d_8): δ 115.61 (s, C_5Me_5), 72.23 (tq, $^1J_{CH}$ = 136.0 Hz, $^3J_{CH}$ = 5 Hz, $^2J_{YC}$ = 5 Hz, $YOCH_2CH_2OY$), 11.28 (s, C_5Me_5). Anal. Calcd for $C_{50}H_{80}O_4Y_2$(THF): C, 65.18; H, 8.91; Y, 17.87. Found: C, 65.08; H, 8.99; Y, 17.69. Crystal data for **8**: $C_{50}H_{80}O_4Y_2$(THF), M = 995.10, orthorhombic with a = 21.7483(12) Å, b = 14.2806(12) Å, c = 16.762(2) Å, V = 5194.7(8) Å^3, space group *Pbcn*, Z = 4, μ(Mo Kα) = 22.8 cm^{-1}. Anisotropic least-squares refinement based on 4163 reflections converged to R_1 = 0.063 and wR_2 = 0.144 for 332 refined parameters.

NMR Tube Reaction of 1a with Furan. To a suspension of 0.019 g (0.026 mmol) of **1a** in 0.5 mL of cyclohexane-d_{12} was added 3.8 μL (0.053 mmol) of furan. Immediately evolution of a gas was observed and **1a** dissolved completely. The solution was transferred to an NMR tube and ^{1}H-NMR showed the complete conversion of **1a** to **9**. ^{1}H-NMR (200 MHz, cyclohexane-d_{12}) δ 7.49 (m, 1H, H5), 6.27 (broad s, 2H, H3 and H4), 1.79 (s, 30H, C_5Me_5).

$Cp^*_2Y(2\text{-}OC_4H_3)(THF)_2$ (10). To a stirred suspension of 1.50 g (2.56 mmol) of $Cp^*_2Cl(LiCl)(Et_2O)_2$ in 35 mL of Et_2O was added 4.10 mL of a 0.620 M solution (2.54 mmol) of 2-lithiofuran in THF. The reaction mixture turned yellow within several minutes. After 1.5 h volatiles were removed under vacuum and the solid was stripped with pentane. Extraction with 20 mL of pentane, concentration and cooling to -30 °C gave 0.354 g (0.620 mmol, 24 %) yellow crystals. IR (cm^{-1}): 1543 (w), 1173 (m), 1117 (m), 1045 (s), 1003 (s), 916 (s), 891 (s), 831 (m), 795 (m), 710 (s), 590 (s). ^{1}H-NMR (300 MHz, benzene-d_6): δ 7.48 (m, 1H, H5), 6.51 (m, 1H, H3 or H4), (pseudo d, J = 2.9 Hz, 1H, H3 or H4), 3.41 (m, 8H, α-THF), 2.16 (s, 30H, C_5Me_5), 1.29 (m, 8H, β-THF). ^{13}C-NMR (75.4 MHz, benzene-d_6): δ 210.09 (d, $^1J_{CY}$ = 62 Hz, C2), 142.35 (ddd, $^1J_{CH}$ = 193 Hz, J = 13 Hz, J = 6 Hz, C5), 119.55 (d, $^1J_{CH}$ = 166 Hz, C3), 116.50 (s, C_5Me_5), 110.05 (ddd, $^1J_{CH}$ = 170 Hz, J = 14 Hz, J = 6 Hz, C4), 68.21 (t, $^1J_{CH}$ = 147 Hz, α-THF), 25.32 (t, $^1J_{CH}$ = 133 Hz, β-THF), 11.89 (q, $^1J_{CH}$ = 126 Hz, C_5Me_5). Elemental analysis was hindered by THF dissociation.

NMR Tube Reaction of 1a with Vinyl Ethyl Ether. In an NMR tube 0.030 g (0.042 mmol) of **1a** was added to a mixture of 8.0 μL (0.083 mmol) of vinyl ethyl ether and 0.5 ml of benzene-d_6. Upon addition of **1a** the solution turned yellow. ^{1}H-NMR after 20 min at room temperature showed the formation of **2a** in quantitative yield.

Reaction of 1a with Vinyl Ethyl Ether: Gas Analysis and GC/MS Analysis. A mixture of 210 μL (2.20 mmol) vinyl ethyl ether and 4.3 mL of toluene was condensed on 0.270 g (0.375 mmol) of **1a** at -196 °C. The mixture was allowed to reach room temperature with stirring during which the solution turned yellow. After stirring for 15 h, gasses were collected by Töpler pump and analyzed by GC: 0.03 mmol ethylene (0.04 mol/mol Y). The remaining volatiles were removed in vacuum and identified as toluene and vinyl ethyl ether by GC. The yellow residue was identified as **2a** by ^{1}H-NMR. The solid was dissolved in 10 mL of toluene and then 250 μL of methanol and 150 μL of water were added. The liquid was dried over $MgSO_4$ and filtrated. GS/MS analysis showed the presence of C_{16}-C_{22} alkanes with exclusively even number of carbon atoms.

NMR Tube Reaction of 1a with Allyl Ethyl Ether. 18.0 mg (0.025 mmol) of **1a** was dissolved in 0.5 mL of benzene-d_6 and 64 μL (0.56 mmol) allyl ethyl ether was added upon which the solution turned yellow. After 5 min at room temperature ^{1}H-NMR showed that **1a** had completely been converted to the allyl ethyl ether adduct of **2a** (57 %) and some unidentified products.

Reaction of 1a with Allyl Ethyl Ether: Gas Analysis. On a vacuum line 10 mL of toluene and 50 μL (0.44 mmol) of allyl ethyl ether were condensed on 0.133 g (0.185 mmol) of **1a** at -196 °C. The reaction mixture was stirred at room temperature for 15 min and the gasses evolved were pumped off through a cold trap at -80 °C and analyzed as 0.046 mmol propane (0.12 mol/mol Y) and 0.162 mmol of propene (0.44 mol/mol Y) by GC.

($Cp^*_2Y)_2(\mu$-O) (11a). On a vacuum line, a bulb containing 0.986 g (1.37 mmol) of **1a** was evacuated. Next, 20 mL of cyclohexane and 140 μL (1.35 mmol) Et_2O were condensed on the solid at -196 °C. After stirring for 0.5 h at room temperature, the gasses evolved were collected by Töpler pump and analyzed by

GC: 1.34 mmol ethane (0.49 mol/mol Y). After stirring for 4 d at 80 °C the gasses evolved were collected and analyzed: 1.29 mmol ethane (0.47 mol/mol Y). Volatiles were removed in vacuum and crystallization from THF afforded 0.703 g (0.957 mmol, 70 %) of colorless crystals. IR (cm^{-1}): 2900 (s), 2726 (w), 1460 (s), 1377 (s), 1306 (w), 1150 (m), 1067 (w), 1020 (m), 723 (m), 658 (s), 625 (m), 590 (w). ^{1}H-NMR (300 MHz, benzene-d_6): δ 2.02 (s, C_5Me_5). ^{13}C-NMR (75.4 MHz, benzene-d_6): δ 117.6 (s, C_5Me_5), 12.06 (q, $^1J_{CH}$ = 124 Hz, C_5Me_5). Anal. Calcd for $C_{40}H_{60}OY_2$: C, 65.39; H, 8.23; Y, 24.20. Found: C, 65.05; H, 8.36; Y, 23.21. MS (EI, 70 eV): *m/e* 734 (M^+).

NMR Tube Reaction: $(Cp^*_2La)_2(\mu$-O) (11b). In an NMR tube 0.014 g (0.017 mmol) of **1b** was dissolved in 0.5 mL of cyclohexane-d_{12} and 1.8 μL (0.017 mmol) of Et_2O was added. In 24 h at 80 °C colorless crystals were formed. In the ^{1}H-NMR spectrum resonances of **11b** and ethane (δ = 0.84) were observed. ^{1}H-NMR (300 MHz, cyclohexane-d_{12}): δ 1.95 (s, C_5Me_5). The NMR tube was opened and volatiles were removed in vacuum. The residue was dissolved completely in THF-d_8. ^{1}H-NMR (300 MHz, THF-d_8): δ 1.99 (s, C_5Me_5).

NMR Tube Reaction: $(Cp^*_2Ce)_2(\mu$-O) (11c). In an NMR tube 0.021 g (0.025 mmol) of **1c** was dissolved in 0.5 mL of cyclohexane-d_{12} and 3.5 μL (0.034 mmol) of Et_2O was added. The reaction was monitored by ^{1}H-NMR. After 24 h at room temperature the Et_2O was completely converted to Cp^*_2CeOEt and ethane (δ = 0.84 ppm) was observed. ^{1}H-NMR for Cp^*_2CeOEt (90 MHz, cyclohexane-d_{12}): δ 26.9 (s, $\Delta\nu_{1/2}$ = 150 Hz, 2H, $CeOCH_2$), 7.62 (s, $\Delta\nu_{1/2}$ = 100 Hz, 3H, $CeOCH_2CH_3$), 1.93 (s, $\Delta\nu_{1/2}$ = 50 Hz, 30 H, C_5Me_5). In 24 h at 80 °C green crystals were formed. Volatiles were removed in vacuum and the residue was redissolved in THF-d_8 upon which a yellow solution formed. ^{1}H-NMR showed resonances which were assigned to $Cp^*_2CeOEt(THF\text{-}d_8)$ and $(Cp^*_2Ce)_2(\mu\text{-}O)(THF\text{-}d_8)_2$ (1.1 : 1.0). ^{1}H-NMR for $Cp^*_2CeOEt(THF\text{-}d_8)$ (300 MHz, THF-d_8): δ 22.48 (s, 2H, $CeOCH_2$), 6.26 (s, 3H, $CeOCH_2CH_3$), 2.24 (s, 30H, C_5Me_5). ^{1}H-NMR for **11c** (300 MHz, THF-d_8): δ 3.54 (s, $\Delta\nu_{1/2}$ = 15 Hz, C_5Me_5).

NMR Tube Reaction of 1a with Me_2S. To a suspension of 30.4 mg (0.0422 mmol) of **1a** in 0.5 mL cyclohexane-d_{12} was added 6.2 μL (0.085 mmol) of Me_2S. Immediately after addition gas evolution was observed and **1a** dissolved. The reaction mixture was transferred to an NMR tube and the tube was sealed under

vacuum. The ^{1}H-NMR spectrum after 1/2 h at room temperature showed that **12** (75 %) and an unidentified compound had been formed. When performed with an excess Me_2S (Me_2S : Y = 10) this unidentified product was absent. ^{1}H-NMR of **12** (200 MHz, cyclohexane-d_{12}): δ 2.21 (s, 3H, SMe), 1,91 (s, 30H, C_5Me_5), 1.33 (broad s, 2H, YCH_2). ^{1}H-NMR of unidentified compound (200 MHz, cyclohexane-d_{12}): δ 1.94 (s, C_5Me_5).

$Cp^*_2YCH_2SMe(THF)$ (13). To a stirred suspension of 0.53 g (0.74 mmol) of $(Cp^*_2YH)_2$ in 20 mL of pentane was added 108 μL (1.5 mmol) of Me_2S. Gas evolution was observed and $(Cp^*_2YH)_2$ dissolved completely. After 10 min at room temperature the orange solution was cooled to -30 °C affording 0.50 g of pink crystals. The pink material was recrystallized from and washed with pentane/THF (2/1) affording 0.31 g (0.63 mmol, 43 %) of white crystals. IR (in cm^{-1}): 2726 (m), 2672 (w), 1303 (m), 1169 (w), 1157 (w), 1015 (m), 970 (w), 864 (m), 839 (m), 721 (m). ^{1}H-NMR (200 MHz, benzene-d_6): δ 3.44 (m, 4H, α-THF), 2.27 (s, 3H, SMe), 2.03 (s, 30H, C_5Me_5), 1.23 (m, 4H, β-THF), 1.19 (d, $^2J_{HY}$ = 2.6 Hz, 2H, YCH_2). ^{13}C-NMR (75.4 MHz, benzene-d_6): δ 116.88 (s, C_5Me_5), 69.79 (t, $^1J_{CH}$ = 149 Hz, α-THF), 37.69 (td, $^1J_{CH}$ = 123 Hz, $^1J_{CY}$ = 46 Hz, YCH_2), 25.97 (q, SMe, overlaps with β-THF), 25.27 (t, $^1J_{CH}$ = 131 Hz, β-THF), 11.37 (q, $^1J_{CH}$ = 126 Hz, C_5Me_5). Anal. Calcd for $C_{26}H_{43}OSY$: C, 63.40; H, 8.80; Y, 18.05. Found: C, 63.40; H, 8.77; Y, 18.25.

NMR Tube Reaction of 1a with Benzyl Methyl Sulfide. To a solution of 0.015 g (0.020 mmol) of **1a** was added 5.5 μL (0.040 mmol) of benzyl methyl sulfide. Immediately gas evolution was observed and a color change to yellow. ^{1}H-NMR after 40 min at room temperature showed the essentially quantitative formation of **14**. ^{1}H-NMR (300 MHz, cyclohexane-d_{12}): 7.21 (m, 1H, aryl H), 6.94 (m, 3H, aryl H), 6.64 (m, 1H, aryl H), 3.43 (d, $^2J_{HY}$ = 3.0 Hz, 1H, YCH), 2.19 (s, 3H, SMe), 2.03 (s, 15H, C_5Me_5), 1.74 (s, 15H, C_5Me_5).

$Cp^*_2YSEt(THF)$ (16). To a stirred suspension of 1.50 g (2.08 mmol) of **1a** in 50 mL of pentane, 0.95 mL (8.8 mmol) of Et_2S was added. After 6 days at room temperature a red solution with a yellow precipitate was formed and volatiles were removed in vacuum. The solid was washed with 50 mL pentane. The residue was dissolved in 5 mL of THF and cooling afforded 0.550 g (1.12 mmol, 27 %) of **16** as white crystals. IR (in cm^{-1}): 2724 (w), 1244 (s), 1014 (s), 959 (w), 918 (w), 860

(s), 766 (w), 665 (m), 592 (w). ^{1}H-NMR (200 MHz, THF-d_8) δ 2.70 (q, $^3J_{HH}$ = 7.3 Hz, 2H, SCH_2), 1.96 (s, 30H, C_5Me_5), 1.19 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_2CH_3). ^{13}C-NMR (75.4 MHz, THF-d_8) δ 119.09 (s, C_5Me_5), 24.99 (t, $^1J_{CH}$ = 136 Hz, SCH_2CH_3), 23.20 (q, $^1J_{CH}$ = 125 Hz, SCH_2CH_3), 12.85 (q, $^1J_{CH}$ = 125 Hz, C_5Me_5). Anal. Calcd for $C_{26}H_{43}OSY$: C, 63.40; H, 8.80; Y, 18.05. Found: C, 63.30; H, 8.81; Y, 18.14.

$Cp^*_2Y(2\text{-}SC_4H_3)(THF)$ (18). 0.876 g (1.22 mmol) of $(Cp^*_2YH)_2$ was suspended in 30 mL of pentane and 200 μL (2.38 mmol) thiophene was added with stirring. Immediately gas evolution was observed along with the formation of a white solid. Volatiles were removed in vacuum and the pink residue was washed three times with 5 mL of pentane. Recrystallization from THF afforded 0.900 g (1.75 mmol, 72 %) of white crystals. IR (cm^{-1}): 3084 (m), 3050 (s), 2957 (s), 2926 (s), 2917 (s), 2857 (s), 2722 (m), 1759 (w), 1559 (w), 1458 (s), 1377 (s), 1343 (m), 1316 (w), 1294 (m), 1246 (w), 1188 (m), 1144 (w), 1063 (m), 1017 (s), 955 (w), 920 (m), 864 (s), 843 (sh), 820 (m), 812 (m), 729 (m), 683 (s), 615 (w), 592 (m), 476(m). ^{1}H-NMR (300 MHz, THF-d_8): δ 7.38 (d, $^3J_{HH}$ = 4.4 Hz, 1H, H5), 7.04 (dd, $^3J_{HH}$ = 4.2 Hz, $^3J_{HH}$ = 3.1 Hz, 1H, H4), 6.81 (d, $^3J_{HH}$ = 2.9 Hz, 1H, H3), 1.79 (s, 30H, C_5Me_5). ^{13}C-NMR (75.4 MHz, THF-d_8): δ 180.24 (d, $^1J_{CY}$ = 62 Hz, C2), 133.68 (ddd, $^1J_{CH}$ = 159 Hz, $^3J_{CH}$ = 12 Hz, $^2J_{CH}$ = 6 Hz, C3), 128.24 (dt, $^1J_{CH}$ = 180 Hz, $^2J_{CH}$ = $^3J_{CH}$ = 9 Hz, C5), 127.16 (dt, $^1J_{CH}$ = 143 Hz, $^2J_{CH}$ = 7 Hz, C4), 118.05 (s, C_5Me_5), 11.72 (q, $^1J_{CH}$ = 126 Hz, C_5Me_5). Anal. Calcd for $C_{28}H_{41}OSY$: C, 65.35; H, 8.03; S, 6.23; Y, 17.28. Found: C, 65.46; H, 8.08; S, 5.32; Y, 17.28.

NMR Tube Reaction of 1a with Allyl Methyl Sulfide. To a suspension of 0.016 g (0.022 mmol) of **1a** in 0.5 mL of cyclohexane-d_{12} was added 5.0 μL (0.046 mmol) of allyl methyl sulfide. ^{1}H-NMR (300 MHz) after 5 min at room temperature showed that 53 % of **19** had been formed along with some unidentified products and unreacted allyl methyl sulfide. For NMR data see text.

Hydrogenation of Allyl Methyl Sulfide. To a suspension of 0.016 g (0.022 mmol) of **1a** in 0.5 mL of cyclohexane-d_{12} under H_2 (1 bar) was added 50 μL (0.46 mmol) of allyl methyl sulfide. ^{1}H-NMR after stirring for 4 d at room temperature showed that 30 % of the allymethylsulfide had been converted to *n*-propyl methyl

sulfide (3.1 mol/mol Y) while the remaining allyl methyl sulfide was present unreacted.

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[12] Formation of this adduct can be explained by fast H/D scrambling between the solvent benzene-d_6 and **1a**, see reference 11 and chapter 2.

[13] There are 3 other resonances in the Cp* area (δ = 2.1-1.9 ppm). Assignment is not well possible but products originating from secondary ether splitting or from metallation on the α-position of the complexed THF followed by enolate formation have to be reckoned with. See also reference 7d.

[14] Also a minor amount of dihydrogen (< 0.05 mol/mol Y) was detected. This can be attributed to conversion of **1a** to the bridged fulvene hydride $Cp^*_2Y(\mu\text{-}H)(\mu\text{-}Fv)YCp^*$[11] but metallation of 1,4-dioxane cannot be excluded.

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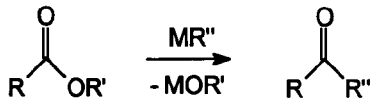
Chapter 6

Reaction of $(Cp^*_2LnH)_2$ (Ln = Y, La) and $Cp^*_2Y(2\text{-}C_6H_4CH_2NMe_2)$ with Esters and Amides. Molecular Structure of $[Cp^*_2Y)_2(\mu\text{-}OCMe{=}CHC(OEt)O)]_2$

Introduction

The recent interest in the use of organolanthanides for organic synthesis[1] has led to the discovery of some useful C-C bond formation reactions mediated by these complexes. For instance aldol coupling of enolizable ketones could be induced by $Cp^*_2LnCH(SiMe_3)_2$ as has been found by Heeres.[2] Samarium based C-C bond forming reactions with aldehydes, ketones and acid chlorides have been reported by Kagan *et al.* and have a broad scope.[3] Recently, interesting work on stereoselective aldol condensations using lanthanide alkoxides has been published.[4]

In this study we focus on the reactions of $(Cp^*_2LnH)_2$ (Ln = Y (**1a**), La (**1b**)), and the intramolecularly stabilized aryl $Cp^*_2Y(2\text{-}C_6H_4CH_2NMe_2)$ (**2**)[5] with esters and amides since condensation of these compounds by yttrium or lanthanide complexes is to our knowledge unprecedented. The intramolecularly stabilized aryl complex was chosen because of the lower steric congestion at the yttrium center compared to that in $Cp^*_2YCH(SiMe_3)_2$.[6] Esters are especially interesting because of the possible addition-elimination sequence depicted in eq 1, which would lead to the alkylation of esters to produce ketones. Another possibility would be enolization of the ester leading to Claisen type condensation with a second equivalent of ester. In addition, we are interested in the effect of the intramolecularly coordinated amine function of **2** on its reactivity.



(1)

This work has been performed in collaboration with F. Wierda. The X-ray structure determination was performed by A. Meetsma.

Results and Discussion

Activation of Esters and Amides by $(Cp^*_2LnH)_2$ (Ln = Y (1a) and La (1b)). Both hydrides **1a** and **1b** reacted with ethyl acetate to form rapidly the alkoxide complexes Cp^*_2LnOEt (Ln = Y (**3a**) and La (**3b**)) through a reductive ester cleavage (eq 2). Even at -80 °C no intermediates could be detected (^{1}H-NMR). With ethyl benzoate an analogous ester cleavage was observed resulting in a 1 : 1 mixture of alkoxides **3** and **4** (eq 3). No metallation of the phenyl ring takes place, which is remarkable when compared with other functionalized arenes PhX (X = OMe, SMe, NMe_2, CH_2NMe_2, PMe_2, PPh_2=CH_2) which are metallated very easily in the ortho position by the same system.[7] It is clear that activation of the carbonyl group by nucleophilic attack of the hydride ligand is the dominant reaction taking place here.

$$\underset{\mathbf{1}}{(Cp^*_2LnH)_2} + MeCOOEt \longrightarrow 2\ \underset{\mathbf{3}}{Cp^*_2LnOEt} \quad (2)$$

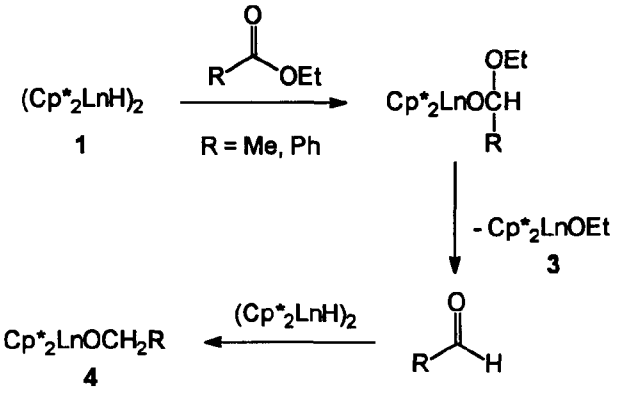
$$\underset{\mathbf{1}}{(Cp^*_2LnH)_2} + PhCOOEt \longrightarrow \underset{\mathbf{3}}{Cp^*_2LnOEt} + \underset{\mathbf{4}}{Cp^*_2LnOCH_2Ph} \quad (3)$$

The first step in the ester reduction is most likely insertion of the carbonyl group in the Ln-H bond as has been observed for **1b** with di-*t*-butyl ketone to form $Cp^*_2LaOCH(^tBu)_2$[2b] (Scheme I). Elimination of the ethoxy group and formation of **3a** and aldehyde HC(O)R seems to be a plausible second step. The aldehyde formed can then be attacked by another molecule of **1** to form $Cp^*_2LnOCH_2R$.

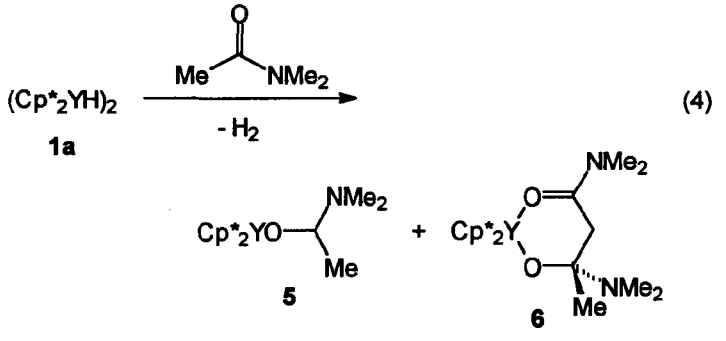
To test whether activation of the carbonyl group is still the main reaction with α, β-unsaturated esters, **1a** and **1b** were allowed to react with ethyl acrylate. This resulted in fast polymerization of the acrylate whereas the bulk of **1a** or **1b** remained intact. This indicates that only minor amounts of **1a** and **1b** are involved in the catalytic polymerization which can be explained by slow initiation. The poly(ethyl acrylate) formed is apparently completely atactic as follows from the ^{1}H-NMR spectrum, which shows two types of methylene and methine protons.[8] However, it is clear that alkoxide formation, which would lead to complete deactivation of the catalyst, is not taking place here. From this it can be concluded that insertion of C-C double bonds into Ln-H can in principle compete successfully with alkoxide elimination. Since polymerization of methyl metacrylate (MMA) has

been investigated extensively[9] we did not look further into this aspect of organo-lanthanide chemistry.

Scheme I

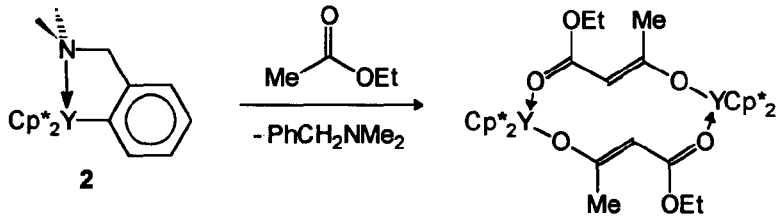


The -NR_2 groups of organic amides are poor leaving groups compared to alkoxy groups of esters. We therefore anticipated that reaction with *N,N*-dimethylacetamide would lead to the carbonyl insertion products of **1a** and **1b**. However the reaction was not clean owing to competitative α-H abstraction and aldol condensation of acetamide (eq 4). This resulted in a mixture of carbonyl insertion product **5** (40 %) and condensation product **6** (60 %). No attempts were made to isolate the aldol coupled product since the reaction of **2** with *N,N*-dimethylacetamide produced **6** in much better yield (*vide infra*).



(4)

Activation of Esters and Amides by $Cp^*_2Y(2\text{-}C_6H_4CH_2NMe_2)$ (2). In contrast to the hydrides **1a** and **1b** which react by nucleophilic attack on the carbonyl function of esters, the aryl **2** behaves like a base and abstracts an α-H of ethyl acetate which subsequently leads to $[Cp^*_2Y(\mu\text{-}OCMe{=}CHC(OEt)O)]_2$ (**7**) as the isolated product (eq 5). Formation of this compound can be explained as follows (Scheme II). The enolate $Cp^*_2YOC(OEt){=}CH_2$, which is formed by α-H abstraction from ethyl acetate, enters a condensation with another molecule of ethyl acetate similar to the mechanism proposed for aldol condensations with $Cp^*_2LnCH(SiMe_3)_2$.2[b] The condensation product then eliminates Cp^*_2YOEt producing a β-keto ester and turning the overall process into a Claisen condensation. The final step is enolization of the β-keto ester by **2** to form **7**.



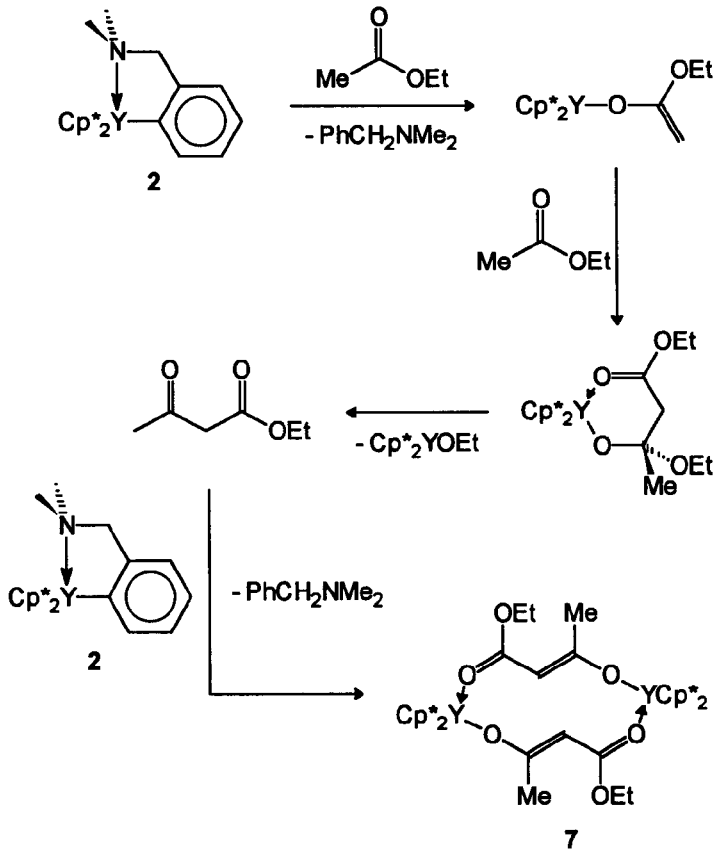
(5)

Compound **7** could be isolated in good yield and was fully characterized. Also the elimination product Cp^*_2YOEt could be detected in the mother liquor as the ethyl acetate adduct after isolation of **7**. The IR spectrum of **7** exhibits a band at 1568 cm^{-1} indicative of a severely reduced carbonyl bond order. Compared to β-keto esters for which $\nu_{C=O}$ occurs at 1650 cm^{-1},[10] this value is significantly shifted to lower frequency. This carbonyl shift can be explained by coordination to the Lewis acidic yttrium center which causes reduction of the carbonyl double bond character. Also the delocalized bonding within the OCMe=CHC(OEt)O causes significant reduction of the C=O bond orde (*vide infra*). The low carbonyl stretching frequency compares well with those observed for tris acetylacetonate complexes $Ln(acac)_3(H_2O)_n$ (1600 cm^{-1}).[11]

The molecular structure of **7** was determined by X-ray diffraction and the resulting geometry is depicted in Figure 1. For selected bond distances and angles see Table I. The molecule is a dimer consisting of two equivalent $Cp^*_2Y(\mu\text{-}OCMe{=}CHC(OEt)O)$ units. The arrangement of the Cp* ligands on yttrium with a Cp*-Y-Cp* angle of 138.6° is normal for bent yttrocene compounds.[12] The Y1-O3a

is significantly longer than the terminal Y-OR distances in the alkoxides $Cp^*Y(OC_6H_3{}^tBu_2)_2$ (2.096(4) and 2.059(3))[13] and $[Cp^*Y(\mu\text{-}O^tBu)(O^tBu)]_2$ (1.995(10) and 2.018(9)).[14] However, the almost linear angle Y1-O3a-C23, which is due to π overlap of the oxygen lone pairs with metal orbitals, was also observed for one of the aryloxy ligands in $Cp^*Y(OC_6H_3{}^tBu_2)_2$. In fact the Y1-O3a distance is intermediate between the Y-O distances in these alkoxides and that of the enolate $[(C_5H_4Me)_2Y(\mu\text{-}OCH_2{=}CH_2)]_2$ (2.275(3) and 2.290(2) Å).[15]

Scheme II



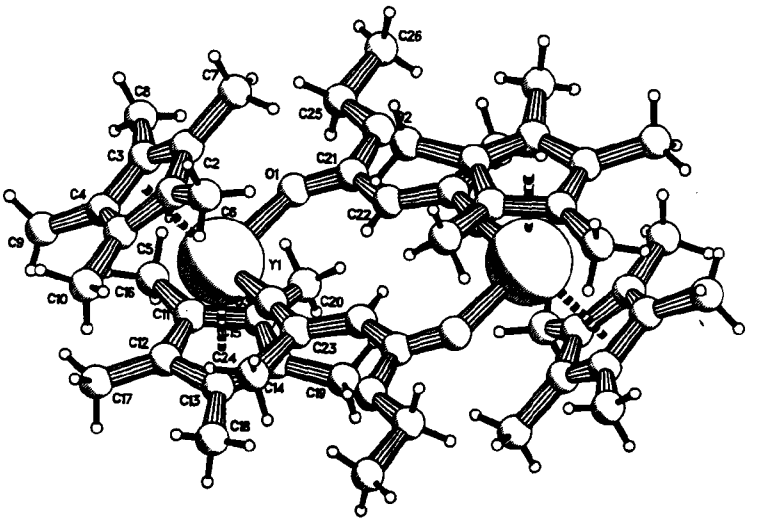


Figure 1. *PLUTO* drawing of $[Cp^*_2Y(\mu\text{-}OCMe{=}CHC(OEt)O)]_2$ (7).

The Y1-O1 distance is significantly longer than Y1-O3a whereas the O1-C21 distance is slightly shorter than O3a-C23. This can be interpreted as a carbonyl function interacting datively with yttrium. The fact that Y1, O1, C21, C22, C23, and O3 lie almost within the same plane, as follows from the torsion angles O3a-Y1-O1-C21, C22-C21-O1-Y1, O1-C21-C22-C23 and C21-C22-C23-O3a, shows that there is significant π overlap between these atoms resulting in delocalized bonding. This is supported by the distances O1-C21, C21-C22, C22-C23, O3-C23 which all indicate significant double bond character (bonding distances for pure double and single bonds: C-C = 1.54 Å, C=C = 1.34 Å, C-O = 1.43 Å, C=O = 1.20 Å).[16] The delocalized bonding within the μ-OCMe=CHC(OEt)O ligands could also explains the elongation of the Y-O3a distance relative to the Y-O distances of $Cp^*Y(OC_6H_3{}^tBu_2)_2$ and $[Cp^*Y(\mu\text{-}O{}^tBu)(O{}^tBu)]_2$.

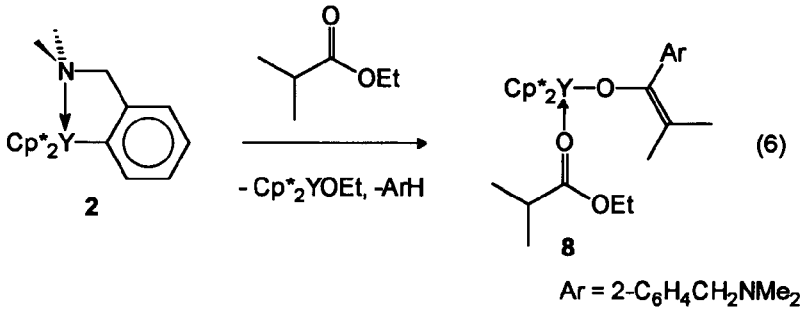
By using a more sterically hindered ester, ethyl-2-methylpropanoate, we tried to isolate the anticipated enolate intermediate. This ester has still one acidic α-H proton but due to the methyl groups in the α-position, nucleophilic attack of the enolate on a second equivalent of ethyl 2-methylpropanoate would be sterically highly unfavorable. However, we did not find the expected enolate complex $Cp^*_2Y(O\text{-}C(OEt){=}CMe_2)$. Instead the product obtained was $Cp^*_2Y(OC(2\text{-}$

$C_6H_4CH_2NMe_2)=CMe_2)(Me_2CHCOOEt)$ (**8**) (eq 6), which could be fully characterized by standard techniques.

Table I. Selected Distances (Å) and Angles (°) for $[Cp^*_2Y(\mu\text{-}OCMe{=}CHC(OEt)O)]_2$ (7).[a]

Y1-O1	2.292(2)	O3a-C23	1.281(4)
Y1-O3a	2.179(2)	C21-C22	1.406(4)
O1-C21	1.260(3)	C22-C23	1.385(3)
O2-C21	1.341(4)	C23-C24	1.513(4)
O2-C25	1.439(4)	C25-C26	1.509(5)
O1-Y1-O3a	103.30(7)	O2-C21-C22	117.9(2)
Y1-O1-C21	137.8(2)	C21-C22-C23	129.3(3)
C21-O2-C25	118.2(2)	O3a-C23-C22	119.8(3)
C23-O3a-Y1a	174.59(18)	O3a-C23-C24	116.8(2)
O1-C21-O2	119.3(3)	C22-C23-C24	123.4(3)
O1-C21-C22	122.8(3)	O2-C25-C26	106.0(3)
Ct1-Y1-Ct2	138.6[b]		
O3a-Y1-O1-C21	6.7(3)	O1-C21-C22-C23	176.7(3)
C22-C21-O1-Y1	-3.6(5)	C21-C22-C23-O3a	177.9(3)

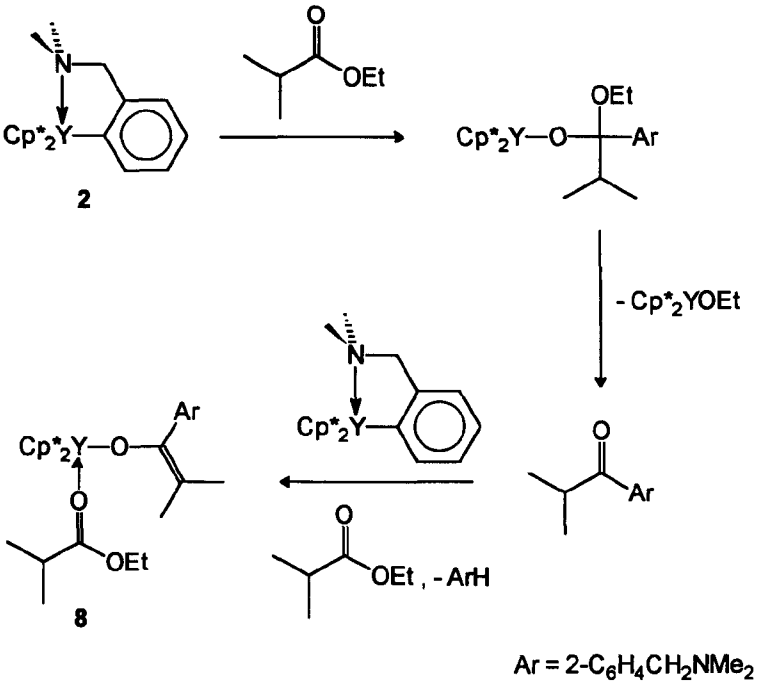
[a] label "a" indicates symmetry operation: -x, -y, 2-z. [b] Ct1 = C1-C5, Ct2 = C11-C15



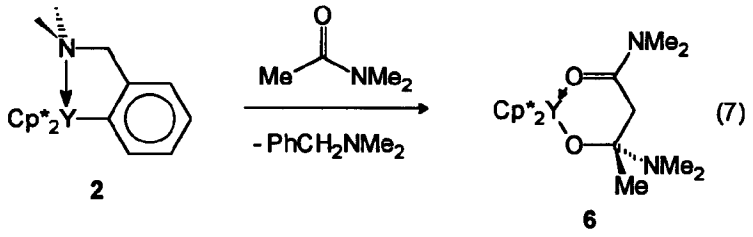
(6)

The presence of the benzyldimethylamine function in **8** suggests that the first step is insertion of the carbonyl function of the ester in the Y-aryl bond of **2** (Scheme III). Next the ethoxy group can be eliminated to form Cp^*_2YOEt and $Me_2CHC(O)C_6H_4CH_2NMe_2$. This is supported by the presence of Cp^*_2YOEt in the reaction mixture (^{1}H-NMR). The ketone produced can then be converted into the enolate by another equivalent of **2** and the final product is formed by complexation of one molecule of ester. This reaction shows that by using a sterically more hindered ester, we have indeed prevented aldol condensation but apparently also the enolization of the ester to $Cp^*_2YOC(OEt)=CMe_2$ is more difficult. Instead, insertion of the carbonyl group of the ester into the Y-aryl bond of **2** is taking place. Although the C-C coupling reaction is now blocked, the OEt elimination, stimulated by the electrophilicity of yttrium, is still possible yielding the observed product **8**.

Scheme III



With *N,N*-dimethylacetamide regular aldol condensation was observed to form $Cp^*_2Y[OC(Me)(NMe_2)CH_2C(O)NMe_2]$ (**6**) (eq 7). In contrast to reaction with **1a** the carbonyl addition product was not formed which indicates that **2** is less nucleophilic and behaves like a base. As stated before, the $-NMe_2$ function is a poor leaving group which prevents NMe_2 elimination and formation of the β-keto amide. Apparently enolization with another equivalent of **2** is more difficult since formation of the enolate is not taking place here.



Concluding Remarks

In this study we have seen that organo-yttrium complexes can function as versatile synthetic tools in organic chemistry. The C-C bond forming aldol and Claisen condensations could offer opportunities for the development of catalysts for these reactions. However, a lot of work needs to be done to reach this goal. In particular the stereochemistry with α-substituted carbonyls needs to be controlled to make these reactions useful in organic synthesis. Therefore, the development of complexes which induce diastereoselective and enantioselective C-C forming condensations remains to be worked out. In this study we have shown that organoyttrium compounds could serve as promising candidates for transformations of this type.

Experimental Section

General Considerations. General procedures, techniques and instrumentation were described in chapters 2 and 4. Compounds **1a**,[6] **1b**,[17] $Li(2\text{-}C_6H_4CH_2NMe_2)$[5a] and $(Cp^*_2YCl)_2$[18] were prepared as described. Reagents ethyl acetate, ethyl benzoate, ethyl acrylate, *N,N*-dimethylacetamide and ethyl 2-methyl propanoate

were distilled and stored over molecular sieves (4 Å). Solvents were distilled from Na/K alloy and degassed prior to use.

Reactions of $(Cp^*_2LnH)_2$ (Ln = Y(1a), La (1b)) with Ethyl Acetate. Ethyl acetate (1.4 μL, 0.015 mmol) was added to a solution of 11 mg (0.015 mmol) **1a** in 0.5 mL of cyclohexane-d_{12}. ^{1}H-NMR spectroscopy after 5 min at room temperature showed the quantitative formation of **3a**. For ^{1}H-NMR data of **3a** see chapter 5. A similar procedure was used for reaction of **1b** with 0.5 equivalent of ethyl acetate per La. Quantitative formation of **3b** was observed within several minutes at room temperature. ^{1}H-NMR (300 MHz, benzene-d_6): δ 3.87 (broad s, $lw_{1/2}$ = 20 Hz, 2H, $LaOCH_2$), 2.07 (s, 30H, C_5Me_5), 1.24 (t, $^3J_{HH}$ = 7.12 Hz, 3H, OCH_2CH_3).

Reactions of $(Cp^*_2LnH)_2$ (Ln = Y (1a), La (1b)) with Ethyl Benzoate. Similar to the reaction of **1a** with ethyl acetate, 1 equivalent of ethyl benzoate per Y was added to a solution of **1a** in cyclohexane-d_{12}. ^{1}H-NMR showed the quantitative formation a 1 : 1 : 1 mixture of **3a**, **4a**, and ethyl benzoate. ^{1}H-NMR for **4a** (200 MHz, cyclohexane-d_{12}): δ 7.60 (d, $^3J_{HH}$ = 7.0 Hz, 2H, ortho H), 7.34 (t, $^3J_{HH}$ = 6.8 Hz, 2H, meta H), 5.36 (s, 2H, OCH_2) 2.07 (s, 30H, C_5Me_5), para H not found due to overlap with signals of unreacted ester. In a similar procedure for **1b**, using 1 equivalent of ethyl benzoate per La, quantitative formation of 1 : 1 : 1 molar mixture of **3b**, **4b** and ethyl benzoate was observed within 5 min at room temperature. ^{1}H-NMR for **4b** (200 MHz, benzene-d_6): δ 7.55 (d, $^3J_{HH}$ = 6.8 Hz, 2H, ortho H), 7.16 (t, $^3J_{HH}$ = 6.8 Hz, 2H, meta H), 5.32 (s, 2H, OCH_2), 2.12 (s, 30 H, C_5Me_5), para H not found due to overlap with signals of unreacted ester.

Reaction of 1a with Ethyl Acrylate. To a solution of 0.025 g (0.035 mmol) of **1a** in 20 mL of cyclohexane was added 1.40 mmol of ethyl acrylate. The reaction mixture was stirred for 2 h at room temperature after which the reaction was quenched with 1 mL of methanol. After the mixture was filtrated and volatiles were removed, a sticky substance remained. ^{1}H-NMR (200 MHz, chloroform-d_1): δ 4.11 (q, $^3J_{HH}$ = 6.8 Hz, OCH_2CH_3), 2.30 (broad s, CH-CH_2-CH), 1.95 (broad s, CH_2-CH-CH_2), 1.65 (broad s, CH-CH_2-CH), 1.52 (broad s, CH_2-CH), 1.25 (t, $^3J_{HH}$ = 6.8 Hz, OCH_2CH_3), relative integrated intensities 4 : 2 : 1 : 2 : 1 : 6 respectively.

Reaction of 1a with *N,N*-Dimethylacetamide. To a stirred solution of 0.20 g (0.28 mmol) of **1a** in 30 mL of pentane was added 104 μL (1.12 mmol) *N,N*-dimethylacetamide. Gas evolution was observed. After 5 min at room temperature stirring was stopped and the mixture was left to crystallize at room temperature. Yield: 0.236 g. ^{1}H- and ^{13}C-NMR showed that this material consisted of **5** (0.23 mmol) and **6** (0.34 mmol). ^{1}H-NMR for **5** (200 MHz, benzene-d_6): 5.01 (q, $^3J_{HH}$ = 5.6 Hz, 1H, OC*H*(Me), 2.35 (s, 6H, NMe_2), 2.14 (s, 30H, C_5Me_5), 1.26 (d, $^3J_{HH}$ = 5.6 Hz, 3H, OCH*Me*). ^{13}C-NMR for **5** (75.4 MHz, benzene-d_6): 114.97 (s, C_5Me_5), 87.61 (dd, $^1J_{CH}$ = 144 Hz, $^2J_{CY}$ = 5 Hz, YOCH), 39.17 (t, $^1J_{CH}$ = 134 Hz, NMe_2), 18.08 (q, $^1J_{CH}$ = 125 Hz, OCH*Me*), 11.68 (q, $^1J_{CH}$ = 125 Hz, C_5Me_5). For NMR data of **6**, see synthesis of this compound from ethyl acetate and **2**.

$Cp^*_2Y(2\text{-}C_6H_4CH_2NMe_2)$ (2). A suspension of 15.9 g (20 mmol) of $(Cp^*_2YCl)_2$ and 5.68 g (40 mmol) of Li-2-$C_6H_4CH_2NMe_2$ in 50 mL of toluene was stirred at room temperature for 15 h. Volatiles were removed in vacuum and the remaining solid was stripped 3 times with pentane. Extraction with pentane and crystallization at -80 °C afforded 9.82 g (20 mmol, 50 %) of **2** as yellow crystals. NMR data were identical to those reported before.[7]

$[Cp^*_2Y(\mu\text{-}OCMe{=}CHC(OEt)O)]_2$ (7). To a stirred solution of 1.13 g (2.29 mmol) of **2** in 20 mL of benzene was added 0.45 mL (4.6 mmol) of ethyl acetate. The mixture was heated to 50 °C for 3 h. Cooling to room temperature gave white crystals which were washed with benzene. Yield: 0.44 g (0.45 mmol, 39 %). IR (cm^{-1}): 1730 (m), 1568 (s), 1537 (m), 1396 (sh), 1323 (m), 1271 (s), 1067 (m), 1020 (m). ^{1}H-NMR (300 MHz, benzene-d_6): δ 5.37 (s, 1H, C=CH), 4.16 (q, $^3J_{HH}$ = 7.0 Hz, 2H, OCH_2), 2.46 (s, 3H, $C(O)CH_3$), 2.01 (s, 30H, C_5Me_5), 1.10 (t, $^3J_{HH}$ = 7.3 Hz, 3H, OCH_2CH_3). ^{13}C-NMR (75.4 MHz, benzene-d_6): δ 190.08 (d, $^2J_{CY}$ = 5 Hz, Y-O-C), 174.01 (d, $^2J_{CY}$ = 2 Hz, Y-O=C), 116.42 (s, C_5Me_5), 91.26 (d, $^1J_{CH}$ = 154 Hz, C=*C*H), 61.14 (t, $^1J_{CH}$ = 145 Hz, OCH_2), 28.23 (q, $^1J_{CH}$ = 127, C(O)*Me*), 14.40 (q, $^1J_{CH}$ = 127 Hz, OCH_2CH_3), 11.06 (q, $^1J_{CH}$ = 126 Hz, C_5Me_5). Anal. Calcd for $C_{26}H_{39}O_3Y$: C, 63.93; H, 8.05; Y, 18.20. Found: C, 63.80; H, 8.29; Y, 18.43. The mother liquor was evaporated to dryness and the residue was identified as $Cp^*_2YOEt(MeCOOEt)$ and traces of **7** by ^{1}H-NMR. ^{1}H-NMR (300 MHz, benzene-d_6): δ 4.19 (q, $^3J_{HH}$ = 6.8 Hz, 2H, $YOCH_2$), 3.97 (q, $^3J_{HH}$ = 7.3 Hz, $C(O)OCH_2$), 2.04 (s, 30H, C_5Me_5), 1.97 (s, 3H,

C(O)Me), 1.32 (t, $^3J_{HH}$ = 6.8 Hz, 3H, $YOCH_2CH_3$), 0.88 (t, $^3J_{HH}$ = 7.3 Hz, 3H, OCH_2CH_3). Crystal data for **7**: $[C_{26}H_{39}O_3Y]_2$, M = 977.00, triclinic with a = 10.129(1) Å, b = 10.650(1) Å, c = 12.093(1) Å, α = 77.642(6)°, β = 79.402(7), γ = 86.408(9), V = 1252.2(2) Å^3, space group $P\bar{1}$, Z = 1, μ(Mo Kα) = 23.6 cm^{-1}. Anisotropic least-squares refinement based on 4871 reflections converged to R_F = 0.034 and wR = 0.041 for 428 refined parameters.

$Cp^*_2Y(OC(2\text{-}C_6H_4CH_2NMe_2)=CMe_2)(Me_2CHCOOEt)$ (8). To a stirred solution of 0.42 g (0.85 mmol) of **2** in 10 mL of toluene was added 250 µL (1.87 mmol) of ethyl 2-methylpropanoate. The reaction mixture was heated at 100 °C for 3 d. Volatiles were evaporated in vacuum and the residue was washed with pentane. Crystallization at -80 °C afforded 0.13 g (0.19 mmol, 22 %) of white crystals. IR (cm^{-1}): 3056 (w), 2780 (m), 2723 (w), 1663 (s), 1642 (s), 1591 (w), 1568 (w), 1536 (w), 1404 (m), 1308 (s), 1292 (s), 1265 (w), 1213 (m), 1196 (m), 1175 (s), 1094 (s), 1068 (w), 1028 (s), 949 (w), 895 (w), 858 (m), 777 (s), 638 (m), 567 (w), 532 (w), 422 (w). ^{1}H-NMR (300 MHz, benzene-d_6): δ 7.83 (d, $^3J_{HH}$ = 7.6 Hz, 1H, aryl H), 7.46 (d, $^3J_{HH}$ = 6.8 Hz, 1H, aryl H), 7.10 (m, 2H, aryl H), 3.79 (m, 4H, overlapping OCH_2 and NCH_2 signals), 2.29 (s, 6H, NMe_2), 2.03 (s, 30H, C_5Me_5), 1.94 (s, 3H, Me), 1.54 (s, 3H, Me), 0.71 (m, 9H, overlapping signals of OCH_2CH_3 and $CHMe_2$), $CHMe_2$ signal not found, presumably due to overlap with the C_5Me_5 signal. ^{13}C-NMR (75.4 MHz, benzene-d_6): δ 184.76 (s, C=O), 151.40 (Y-OC), 143.82 (s, aryl C), 137.95 (s, aryl C), 130.2 (d, $^1J_{CH}$ = 149 Hz, aryl CH), 127.75 (aryl C, overlapping with solvent signal), 126.17 (d, $^1J_{CH}$ = 147 Hz, aryl CH), 116.28 (s, C_5Me_5), 97.25 (s, $=CMe_2$), 62.95 (t, $^1J_{CH}$ = 148 Hz, OCH_2), 61.44 (t, $^1J_{CH}$ = 132 Hz, NCH_2), 46.05 (q, $^1J_{CH}$ = 132 Hz, NMe_2), 35.31 (d, $^1J_{CH}$ = 136 Hz, $CHMe_2$), 20.17 (q, $^1J_{CH}$ = 124 Hz, Me), 19.86 (q, $^1J_{CH}$ = 124 Hz, Me), 19.42 (q, $^1J_{CH}$ = 128 Hz, $CHMe_2$), 13.62 (q, $^1J_{CH}$ = 128 Hz, Me), 11.68 (q, $^1J_{CH}$ = 125 Hz, C_5Me_5), one aryl CH not found due to overlap with solvent signal. Anal.Calcd for $C_{39}H_{60}O_3NY$: C, 68.91; H, 8.90; Y, 13.08. Found: C, 68.11; H, 8.85; Y, 13.74.

$Cp^*_2Y(OC(Me)(NMe_2)CH_2C(O)NMe_2)$ (6). To a stirred solution of 1.33 g (2.69 mmol) of **2** in 10 mL of benzene was added 0.50 mL (5.2 mmol) of *N,N*-dimethylacetamide. The reaction mixture was stirred for 15 h at 50 °C and volatiles were removed in vacuum. The residue was washed with pentane and crystallization from toluene at -80 °C yielded 0.59 g (1.13 mmol, 42 %) of white crystals. IR (cm^{-1}

1): 1606 (s), 1587 (s), 1410 (m), 1325 (m), 1264 (w), 1224 (m), 1215 (m), 1018 (s), 985 (m), 594 (m). ^{1}H-NMR (200 MHz, benzene-d_6): δ 3.21 (s, 2H, C(O)CH_2), 2.77 (s, 6H, NMe$_2$), 2.45 (s, 3H, Me), 2.17 (s, 30H, C$_5$Me$_5$), 1.82 (s, 3H, NMe), 1.80 (s, 3H, NMe). ^{13}C-NMR (75.4 MHz, benzene-d_{12}): δ 167.50 (s, C=O), 115.96 (s, *C*$_5$Me$_5$), 60.99 (t, $^1J_{CH}$ = 155 Hz, C(O)*C*H$_2$), 40.44 (q, $^1J_{CH}$ = 134 Hz, N*Me*$_2$), 37.46 (q, $^1J_{CH}$ = 139 Hz, NMe), 35.98 (q, $^1J_{CH}$ = 140 Hz, NMe), 21.90 (q, $^1J_{CH}$ = 130 Hz, Me), 11.53 (q, $^1J_{CH}$ = 125 Hz, C$_5$*Me*$_5$), Y-O-C carbon not found. Anal. Calcd for $C_{28}H_{47}O_2N_2Y$: C, 63.14; H, 8.89; N, 5.26; Y, 16.69. Found: C, 63.47; H, 8.99; N, 5.44; Y, 17.13.

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Samenvatting

Economische overwegingen en hogere milieu-eisen vormen de drijfveer achter een belangrijke ontwikkeling in de hedendaagse chemie: het zoeken naar processen met extreem hoge selectiviteit. Zowel in de bulk- als in de fijnchemie is er een grote behoefte aan schone processen die weinig bijproducten genereren en doelmatiger gebruik maken van grondstoffen. Katalyse zal een van de meest doeltreffende methoden kunnen zijn om deze doelstelling te realiseren.

C-C koppelingsreacties zijn in synthetisch opzicht erg belangrijk en vaak onderdeel van industriëel toegepaste processen. Vooral vroege-overgangsmetaalcomplexen en in het bijzonder verbindingen van groep 3 metalen en lanthaniden zijn zeer actieve katalysatoren gebleken voor dit type reacties. Echter, ondanks de hoge katalytische activiteit van groep 3 en lanthanidecomplexen, is hun toepasbaarheid beperkt gebleven tot de katalytische omzetting van niet-gefunctionaliseerde olefines. Functionele groepen worden niet of nauwelijks getolereerd en leiden tot deactivering van het katalysatorsysteem. De ontwikkeling van katalysatoren gebaseerd op groep 3 of lanthanide-elementen, die zowel een hoge activiteit hebben als bestand zijn tegen functionele groepen, is daarom een grote uitdaging.

In dit proefschrift wordt de activering van C-H en C-X bindingen door organolanthanide complexen beschreven (X = hetero-atoom). Het doel van dit onderzoek, dat nader uiteengezet wordt in hoofdstuk 1, bestaat uit twee delen: Enerzijds de mechanistische bestudering van C-H activeringsreacties met $(Cp^*_2LnH)_2$ complexen ($Cp^* = \eta^5\text{-}C_5Me_5$, Ln = groep 3 metaal of lanthanide). Anderzijds bestudering van de reacties tussen organolanthanide systemen en hetero-atoom bevattende organische verbindingen. Een beter begrip van dit type reacties draagt bij aan de ontwikkeling van nieuwe katalytische processen gebaseerd op groep 3 en lanthanide complexen.

In eerste instantie werd getracht meer inzicht te verkrijgen in de C-H activering van arenen door het yttrium hydride complex $(Cp^*_2YH)_2$ (hoofdstukken 2 en 3). Gevonden werd dat dit complex actief is in een aantal C-H activeringsreacties waaronder de activering van inert-veronderstelde oplosmiddelen als benzeen en tolueen (hoofdstuk 2). De eerder waargenomen activering van één van de C-H bindingen van een Cp* ligand in $(Cp^*_2YH)_2$, die leidt tot metallering van dit ligand

en de vorming van het fulveen complex $Cp^*_2Y(\mu\text{-}H)(\mu\text{-}\eta^1;\eta^5\text{-}CH_2C_5Me_4)YCp^*$, bleek ook in benzeen en tolueen plaats te vinden. Metallering van het oplosmiddel is echter een concurrerend proces en leidt tot fenyl en benzyl complexen, Cp^*_2YPh en $Cp^*_2YCH_2Ph$. Bovendien is er in benzeen en tolueen sprake van een zeer snelle reactie waarbij waterstofatomen van het areenmolecuul uitwisselen met het hydride waterstofatoom van $(Cp^*_2YH)_2$. In gedeutereerde aromatische oplosmiddelen is dit proces waarneembaar als H/D uitwisseling tussen oplosmiddel en hydride.

De mechanistische verklaring van H/H (H/D) uitwisseling werd onderbouwd met een extended Hückel molecular orbital (EHMO) studie (hoofdstuk 3). Het bleek dat H/D scrambling tussen $(Cp^*_2LnH)_2$ complexen en arenen door een nieuw σ-bond metathese proces beschreven kan worden. Dit proces is zeer specifiek voor arenen en houdt verband met het aromatisch π-systeem van deze moleculen.

Vervolgens werd de aandacht gericht op activering van hetero-atoom bevattende moleculen. In hoofdstuk 4 wordt nader ingegaan op de activering van pyridine, de vorming van het metalleringsproduct $Cp^*_2Y(2\text{-pyridyl})$ en de chemie van deze laatste verbinding. Een aantal interessante functionaliseringen van pyridine kon worden bewerkstelligd, waarbij het pyridine-stikstofatoom als een richtende groep functioneerde. In het bijzonder de insertiereactie van koolmonoxide met $Cp^*_2Y(2\text{-pyridyl})$ was opmerkelijk en leidde tot de vorming van $(Cp^*_2Y)_2(\mu\text{-}\eta^2;\eta^2\text{-}OC(2\text{-}NC_5H_4)_2)$. Deze verbinding is het resultaat van twee C-C koppelingsreacties tussen CO en twee pyridylliganden. Uitgaande van $Cp^*_2Y(2\text{-pyridyl})$ en etheen of propeen, werden mono-insertieproducten gevormd. Het etheen-insertieproduct $Cp^*_2YCH_2CH_2(2\text{-}NC_5H_4)$ bleek actief als katalysator voor de omzetting van etheen en pyridine in 2-ethylpyridine. Tevens werd een opmerkelijke C-C koppelingsreactie tussen $Cp^*_2Y(2\text{-pyridyl})$ en pyridine gevonden wat resulteerde in de vorming van 2,2'-bipyridine. Deze omzetting bleek echter niet katalytisch te zijn.

Ethers en organische sulfides kunnen eveneens gemakkelijk geactiveerd worden door $(Cp^*_2LnH)_2$ complexen (hoofdstuk 5). Er bleek in veel gevallen een delicate balans te zijn tussen C-H en C-X activering. Terwijl voor ethers C-O splitsing de voornaamste reactieroute is, werd voor sulfides hoofdzakelijk selectieve metallering waargenomen. Dubbele ethersplitsing in 1,4-dioxaan leidde tot vorming van het glycolaatcomplex $(Cp^*_2Y)_2(\mu\text{-}OCH_2CH_2O)(THF)_2$ en afsplitsing van ethaan.

Ook voor gewone ethers werd onder bepaalde omstandigheden dubbele C-O activering waargenomen en dit leidde tot vorming van oxo-complexen $(Cp^*_2Ln)_2(\mu\text{-}O)$ en alkaan. De belangrijkste conclusie is dat olefines met etherfuncties in

katalytische hydrogenering en polymerisatie gemakkelijk deactivering van het katalysatorsysteem kunnen geven door C-O bindingssplitsing en vorming van niet katalytisch actieve alkoxides en oxides.

Tenslotte werd de activering van esters en amides bestudeerd (hoofdstuk 6). Met de hydride complexen $(Cp^*_2LnH)_2$ (Ln = Y, La) bleek reductieve splitsing van esters op te treden terwijl amides zowel insertie als aldolkoppeling ondergingen. De arylverbinding $Cp^*_2Y(2\text{-}C_6H_4CH_2NMe_2)$ induceerde Claisen- en aldolcondensaties van respectievelijk esters en amides. Deze C-C koppelingsreacties bieden aantrekkelijke perspectieven voor de toepassing van organolanthanides in de organische synthese.

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